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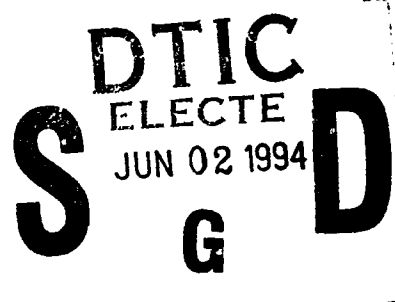
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Chemically Modified Electrodes

by

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13. ABSTRACT (Maximum 200 words)

We learn that the field of chemically-modified electrodes involves attaching specific molecules to the surfaces of conventional "inert" electrodes. We also discover the two major reasons for wanting to attach molecules to electrode surfaces. One objective is to obtain fundamental information about the mechanism of electron transfer at electrode surfaces. The second objective is to impart to the electrode surface some chemical specificity not available at the unmodified electrode. For example, the modified electrode might catalyze a specific chemical reaction. Alternatively, the modified electrode might be able to recognize a specific molecule present in a contacting solution phase.

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Chemically Modified Electrodes

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"Thus, when a substituent of interest is incorporated into an olefinic substance and the resulting compound allowed to react with the electrode surface, the substituent becomes connected to the surface......By this means, ionic species have been tethered within the double layer region in order to probe the mechanisms of electrode reactions involving platinum complexes......Alternatively, the electrochemical reactant itself can be connected to the electrode surface, allowing its reactivity to be observed as a function of charge, orientation, and structure, as described here."

R.F. Lane and A.T. Hubbard, *Journal of Physical Chemistry*, Vol. 77, p. 1401, 1973.

"If a method for securely anchoring such molecules could be found, advantage could be taken of the molecular structure to build surfaces with unique and widely varying properties. Indeed, the attached molecules could be used in the sense of chemical reagents to perform reactions in tandem with the electron transfer processes characteristic of chemically inert electrodes."

B.F. Watkins, J.R. Behling, E. Kariv, and L.L Miller, *Journal of the American Chemical Society*, Vol. 97, p. 3549, 1975.

"We see this line of research as eventually leading to a wide array of chemically modified electrode surfaces with unusual analytical, chemical, catalytic and optical properties."

C.M. Elliott and R.W. Murray, *Analytical Chemistry*, Vol. 48, p. 1247, 1976.

I. INTRODUCTION.

These quotes were chosen to introduce this chapter on "chemically-modified electrodes" because they are from some of the earliest papers in the field and because they review the concepts and objectives of this research area. We learn that the field of chemically-modified electrodes involves attaching specific molecules to the surfaces of conventional "inert" electrodes. We also discover the two major reasons for wanting to attach molecules to electrode surfaces. As explained by Lane and Hubbard, one objective is to obtain fundamental information about the mechanism of electron transfer at electrode surfaces. The second objective, as expressed by Miller at al. and Elliott and Murray, is to impart to the electrode surface some chemical specificity not available at the unmodified electrode. For example, the modified electrode might catalyze a specific chemical reaction. Alternatively, the modified

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electrode might be able to recognize a specific molecule present in a contacting solution phase.

It is also of interest to note the age of the above quotes. It has now been 20 years since the publication of the first papers on chemically-modified electrodes. During these 20 years this concept has been the subject of intense research activity. Indeed, it is fair to say that chemically-modified electrodes have been the most popular (important?) research area in electrochemistry during the previous two decades. There are now thousands of papers in the literature on this subject; fortunately, a number of authoritative reviews of this voluminous literature are available (1-8). Because of the importance of this field, it is essential that students of modern electrochemistry have a working knowledge of chemically-modified electrodes. The objective of this chapter is to provide this knowledge.

We first review methods for preparing chemically-modified electrodes. This section is organized roughly according to the chronology of development of the various types of modified electrodes. We then discuss the fundamentals of electrochemical processes at chemically-modified electrodes. Section IV then provides a discussion of methods used for characterizing chemically-modified electrodes. Both electrochemical and spectroscopic methods are reviewed. The penultimate section then describes potential applications of these devices. Applications in both fundamental and applied science are reviewed. We conclude with some highly-biased observations about the impact of this field and where this field is going.

II. METHODS FOR PREPARING CHEMICALLY MODIFIED ELECTRODES.

There are now over a half dozen demonstrated methods for preparing chemically-modified electrodes. These range from simple chemisorption to electrosynthesis of a polymer film at an electrode surface. We review five methods here.
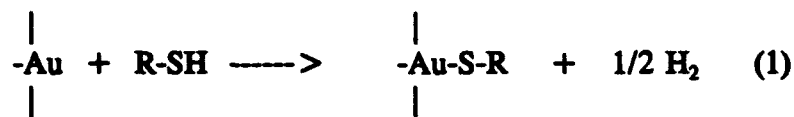
A. <u>Methods based on chemisorption</u>. Chemisorption (9) is an adsorptive interaction between a molecule and a surface in which electron density is shared by the adsorbed molecule and the surface. Electrochemical investigations of molecules that are chemisorbed to electrode surfaces have been conducted for at least three decades. Why is it, then, that the papers that are credited with *starting* the chemically-modified electrode field (in 1973) describe chemisorption of olefinic substances on platinum electrodes (10,11)? What is it about these papers that is different from the earlier work? The answer to this question lies in the quote by Lane and Hubbard at the start of this chapter. Lane and Hubbard raised the possibility of using carefully-designed adsorbate molecules to probe the fundamentals of electron-transfer reactions at electrode surfaces. It is this concept of specifically tailoring an electrode surface to achieve a particular desired goal that distinguishes this work from the prior literature on chemisorption and it is this concept that launched the chemically-modified electrode field.

Since the pioneering work of Lane and Hubbard, there have been numerous examples of using chemisorption to modify electrode surfaces. For example, Anson and his coworkers have investigated chemisorption of various aromatic systems onto carbon electrodes (12). In this case, π electron density is shared between the electrode and the adsorbate molecule. Examples of electroactive molecules that have been used to modify electrode surfaces via this approach are shown in Table I (8). It is of interest to note that from the very beginning, there was considerable interest in modifying electrode surfaces with biochemical substances (Table I). This is because such modified electrodes seemed to be likely candidates for use in electrocatalytic processes and biochemical sensors (see Applications section).

Chemisorption requires direct contact between the chemisorbed molecule and the

electrode surface; as a result, the highest coverage achievable is usually a monomolecular layer. This may be contrasted with several of the methods to be discussed below that allow the electrode surface to be covered with thick films (i.e. multimolecular layers) of the desired molecule. In addition to this coverage limitation, chemisorption is rarely completely irreversible. In most cases, the chemisorbed molecules slowly leach into the contacting solution phase during electrochemical, or other, investigations of the chemisorbed layer. For these reasons, electrode modification via chemisorption was quickly supplanted by other methods, most notably polymer-coating methods.
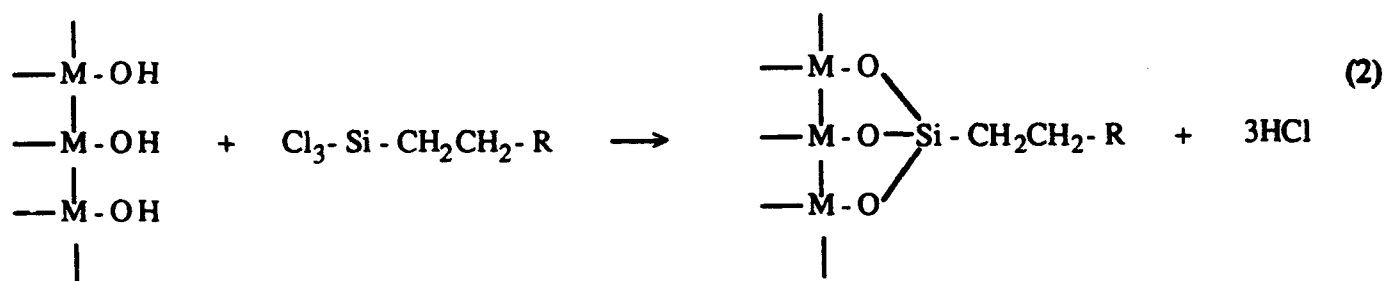
There has, however, been a recent "rebirth" of interest in using chemisorption to modify electrode surfaces. This rebirth is centered around the use of thiols, sulfides, and disulfides as chemisorption agents for derivatization of gold (and other) electrode surfaces (13). In the case of an alkylthiol, this chemisorption reaction can be written as (14)

$$\begin{matrix} | \\ -Au \\ | \end{matrix} + R\text{-}SH \longrightarrow \begin{matrix} | \\ -Au\text{-}S\text{-}R \\ | \end{matrix} + 1/2\ H_2 \quad (1)$$

where Au represents a gold atom at the electrode surface and R is the alkyl substituent. The reaction is typically carried out by simply immersing the electrode into a dilute solution of the thiol. These derivitization agents are of tremendous current interest because this simple chemisorption processes can yield densely-packed and highly-ordered monolayer films on metal surfaces and because the nature of the R group (Equation 1) can be changed at will. These films have been called "self-assembled" monolayers.

B. Methods Based on Covalent Bond Formation. A variety of methods were developed, during the mid and late seventies, for forming covalent bonds between specific functional groups on the

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electrode surface and the molecule to be attached to the surface. The quintessential example involves reaction of a surface hydroxyl with a hydrolytically-unstable silane (15). This chemistry is illustrated in Equation 2 where M-OH represents a hydroxyl group on an electrode surface and R on the silane is the functional group that is to be attached to the electrode surface. Murray and his associates were the first to use this chemistry to modify electrode surfaces. This chemistry has since been used to attach an enormous number of functional groups to SnO_2, RuO_2, TiO_2, Pt, Au, and other electrode surfaces (15).

$$
\begin{array}{c}
| \\
-M-OH \\
| \\
-M-OH \quad + \quad Cl_3-Si-CH_2CH_2-R \quad \longrightarrow \\
| \\
-M-OH \\
|
\end{array}
\qquad
\begin{array}{c}
| \\
-M-O \\
| \quad \backslash \\
-M-O-Si-CH_2CH_2-R \quad + \quad 3HCl \qquad (2) \\
| \quad / \\
-M-O \\
|
\end{array}
$$

Equation 2 should be viewed as a "cartoon" version of the "silanization" reaction because while the silane is, in principle, capable of forming three covalent bonds to the surface, it is doubtful that all three actually form. Indeed, if traces of water are present, the silane will be hydrolyzed to form a siloxane polymer that will ultimately become covalently attached to the electrode surface. Because a polymer is formed, it is possible to achieve multimolecular layers at the electrode surface via this chemistry. Wrighton et al. have made extensive use of such hydrolytically-unstable silanes to prepare multilayer films containing numerous desired electroactive functionalities (16).

A variety of other surface chemistries have been used to attach chemical species to electrode surfaces. For example, Miller et al. activated the carboxylic acid functionalities on carbon electrodes with thionyl chloride and then reacted this surface with amines (17). Sagiv

and his coworkers have recently invented a clever approach for monolayer-by-monolayer deposition of multilayer films based on organosilane chemistry (18). Finally, Mallouk et al. have also developed a monolayer-by-monolayer approach for synthesizing well-ordered multilayer films (19). Because of these interesting new synthetic strategies, covalent attachment of functional groups remains an attractive approach for modifying electrode surfaces.

C. <u>Coating Electrodes with Polymer Films</u>. In 1978 Miller's group and Bard's group independently showed that chemically-modified electrodes could be prepared by coating electrode surfaces with polymer films (20,21). This has since proven to be the most versatile approach for preparing chemically-modified electrodes. Indeed, until the recent rebirth of chemisorption and new covalent-attachment schemes (see above), the polymer-film method had essentially supplanted all other methods for preparing chemically-modified electrodes.

There are many reasons for the popularity of polymer films as electrode-modifying agents. First, it is easy to prepare multilayer films using the polymer route. Indeed, the quantity of polymer deposited (i.e. the thickness of the film) can be reliably and reproducibly varied. Polymer films can be made completely insoluble in the contacting solution phase; thus, loss of material from the electrode is not a problem. Many organic polymers have tremendous chemical stability (think how long it takes a plastic six-pack ring to degrade); hence, degradation of the film is usually not a problem. Polymers can be prepared in almost infinite variety. Thus, polymers that incorporate any desired electroactive chemical functionality can be synthesized. Finally, other types of functional groups can be easily added to the polymer; for example, ionic groups can be added to increase film conductivity.

An enormous number of polymers have been used to prepare chemically-modified

electrodes. Some examples are given in Table II; Albery and Hillman provide a more extensive list (8). As indicated in Table II, these polymers can be divided into three general categories - redox polymers, ion exchange and coordination polymers, and electronically conductive polymers. Redox polymers are polymers that contain electroactive functionalities either within the main polymer chain or in side groups pendant to this chain. The quintessential example is poly(vinylferrocene) (Table II). The ferrocene groups attached to the polymer chain are the electroactive functionality. Ferrocene can be oxidized by one electron to the cationic ferricinium. If ferrocene is abbreviated Fc and ferricinium is abbreviated Fc^+, this oxidation process can be represented as follows:

$$Fc \quad ---> \quad Fc^+ \quad + \quad e^- \qquad (3)$$

We will have more to say about this electrochemistry in the following section.

Ion exchange and coordination polymers are not, themselves, electroactive but can incorporate electroactive guest molecules. For example, Anson's group showed that films of poly(vinylpyridine) can incorporate *electroactive* coordinatively-unsaturated metal complexes via coordination of the metal to the polymer-bound pyridine (22). Likewise, ion exchange polymers incorporate *electroactive* counterions via an ion exchange reaction. The most extensively-investigated polymer of this type is du Pont's perfluorosulfonate ionomer, Nafion (Table II). Nafion is a strong acid ion exchange polymer. The proton can, therefore, be replaced with an electroactive cation (M^{n+}) via

$$n \ (-SO_3H)_{polym} \ + \ M^{n+}_{soln} \ -----> \ [M^{n+} \ (-SO_3^-)_n]_{polym} \ + \ n \ H^+_{soln} \qquad (4)$$

where the subscript "polym" denotes the polymer phase, and the subscript "soln" denotes a contacting solution phase that contains the exchanging cation. A large number of electroactive

cations can be incorporated into Nafion films at electrode surfaces via this chemistry (23).

Nafion film-coated electrodes have an interesting early history. Such electrodes are prepared by applying a solution of the polymer to the electrode surface. However, prior to 1982 only du Pont knew how to dissolve the polymer, and they gave solutions of this polymer to only two U.S. laboratories. These laboratories showed that this polymer was an extremely interesting and versatile material for preparing chemically-modified electrodes. Unfortunately, no one else could get their hands on the polymer solution! This situation changed dramatically when Martin's group developed a procedure for dissolving the film form of Nafion (24). Shortly thereafter, solutions of this polymer were marketed commercially. Since then, Nafion film-coated electrodes have become the most extensively investigated chemically-modified electrodes. Some examples of these electrodes are presented in the Applications Section.

The third class of polymers used to prepare chemically-modified electrodes is the electronically-conductive polymers (25). The polymer chains in this family of materials are themselves electroactive. For example, the polymer redox reaction for polypyrrole (Table II) can be written as follows:

(5)
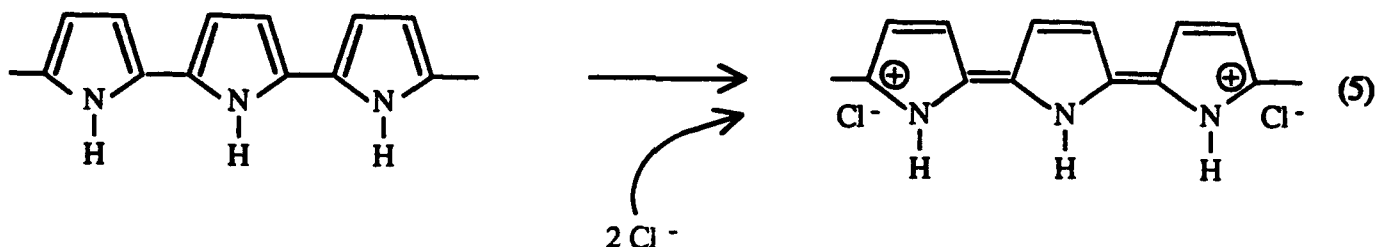
(The charge-balancing (see below) anions come from the contacting electrolyte phase.) Note that because the polymer is conjugated, the cationic site created upon oxidation is delocalized along the polymer chain. This may be contrasted to the case of a redox polymer, such as

poly(vinylferrocene), where the positive charge created upon oxidation is localized within the ferrocene moiety. The delocalization in the conductive polymers causes these polymers to be electronic conductors (i.e. similar to metals) (25). This unique class of materials has generated a tremendous amount of excitement during the last decade and electrochemists have made important contributions to our understanding of these materials. In particular, Arturo F. Diaz at IBM has been instrumental in developing synthetic methods and exploring how structure affects conductivity in these materials (26).

A number of different methods can be used to prepare polymer film-coated electrodes. The simplest is to dip the surface to be coated into a solution of the polymer, remove the electrode from the solution, and allow the solvent to evaporate. While this method is simple, it is difficult to control the amount of material that ends up on the electrode surface. Alternatively, a measured volume of solution can be applied to the surface to be coated. This allows for accurate control of the amount of polymer applied. The polymer film may also be spin-coated onto the electrode surface. Spin-coating is used extensively in the semiconductor industry and yields very uniform film thicknesses.

Polymer films can also be electro-polymerized directly onto the electrode surface. For example, Abruña et al. have shown that vinylpyridine and vinylbipyridine complexes of various metal ions can be electropolymerized to yield polymer films, on the electrode surface, that contain the electroactive metal complex (see Table II) (27). The electronically conductive polymers (Table II) can also be electro-synthesized from the corresponding monomer. Again, a polymer film that coats the electrode surface is obtained (25). Electropolymerized films have also been obtained from styrenic, phenolic, and vinyl monomers.

D. Coating Electrode Surfaces with Inorganic Materials. Clays, zeolites and other inorganic, microcrystalline structured materials have also been used to modify electrode surfaces (28-30). These inorganic materials are of interest because they are ion exchangers, like ion exchange polymers; however, unlike polymers, clays and zeolites can withstand high temperatures and highly-oxidizing solution environments. Furthermore, these inorganic materials have well-defined microstructures. For example, clays have a sheet-like structure and zeolites contain pores and channels of well-defined diameter. Zeolites have long been used as sorbants and catalysts; hence, it only seemed natural to explore the electrochemical properties of electrodes modified with these and related materials. Rollison and her coworkers were the first to explore Zeolite-modified electrodes (29).

A considerable amount of work has also been done on an interesting family of transition metal hexacyanometalates, having the general formula $M_k^A[M^B(CN)_6]_x$ where M^A and M^B are transition metals with different formal oxidation numbers (30). The quintessential member of this family is the material know as Prussian blue, $Fe_4[Fe(CN)_6]_3$. This material has been know since at least the eighteenth century (31) and has, because of its intense blue color, been used extensively as a pigment. This family of materials forms inorganic polymers that can be coated as thin films on electrode surfaces. These films have interesting electrochemical and optical properties. In particular, they display a property called electrochromism - the ability of a material to change its color upon a change in oxidation state. We will discuss an electrochromic device, a "smart window," in the Applications section of this chapter.

Finally, Majda has investigated a novel inorganic membrane-modified electrode (32). The membrane used was a microporous alumina prepared by anodizing metallic aluminum in an

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acidic electrolyte (33). Majda et al. lined the pores of these membranes with polymers and self-assembled monolayers and studied electron and ion transfer down the modified pore walls to a substrate electrode surface (32). Martin and his coworkers have used the pores in such membranes as templates to electrochemically synthesize nanoscopic metal, polymer, and semiconductor particles (34).

E. Langmuir-Blodgett (LB) Methods. In the 1930's Irving Langmuir and Katharine Blodgett invented a method for creating highly-ordered monolayer films at the air/water interface and then transferring these films to substrate surfaces. The LB method entails the use of a molecule with a polar "head group" (e.g. a carboxylate) and a hydrophobic "tail" (e.g. an alkyl chain). When such amphiphilic molecules (called surfactants) are dispersed onto the surface of water, the head groups point down, because they are strongly solvated by water, and the hydrophobic tails point up. The LB method has recently been used to coat electrode surfaces with monolayer and, after multiple transfers, multilayer films (35). In particular, surfactants with electroactive ions as the head group have been used, and the electrochemical and photoelectrochemical properties of the resulting films have been investigated (35). The self-assembly and LB methods can, in principle, produce analogous structures on electrode surface. The self-assembly method seems, however, to be more versatile and, because of the formation of the chemisorptive chemical bond, should produce a more stable film.

III. ELECTROCHEMISTRY AT CHEMICALLY MODIFIED ELECTRODES.

The objective of this section is to give the reader the basics of how electrochemical reactions occur at chemically-modified electrodes. We consider two simple limiting cases. The first is the case of an electroactive monolayer film attached to an electrode surface. The second

is the case of an electroactive polymer film, that is significantly thicker than a monolayer. Polymer films of this type have sometimes been called "multilayer" films because they can be conceptually divided into a collection of monolayers of the polymer stacked one on top of the other. This is an artificial concept because there are no real layers (like the layers in plywood) within the polymer film; however, this concept can be useful in thinking about, and modeling, the electrochemistry of such films.

A. Electrochemistry at a Monolayer Film Coated Electrode. Let us assume that a gold-disk electrode has been coated with a "self-assembled" monolayer (see above) of the following thiol:

$$HS\text{-}(CH_2)_x\text{-}Fc \qquad (6)$$

Clearly, this thiol can be used to attach ferrocene groups (Fc) to the Au electrode surface. If we abbreviate the surface-confined ferrocene group as -Fc, it should be possible to drive the following surface redox reaction:

$$\text{-Fc} \longrightarrow \text{-Fc}^+ + e^- \qquad (7)$$
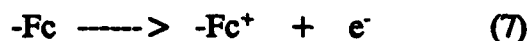
This would be accomplished by immersing the chemically-modified electrode, a reference electrode, and a counter electrode (see Chapter ??) into an appropriate electrolyte solution (e.g. 0.1 M $NaClO_4$ in acetonitrile). The potential difference between the modified electrode (the working electrode) and the reference would then be adjusted to a value appropriate to drive the above reaction, using a commercially-available potentiostat, and the resulting anodic current would be measured.

A schematic drawing of this surface-confined oxidation process is shown in Figure 1. Note that the film is represented as a rather disordered monomolecular layer of attached -Fc groups. Initially all of these groups are in the unoxidized -Fc state (Figure 2A); however, upon

application of a suitably-positive potential to the working electrode, these -Fc sites give up their electrons to the substrate electrode (Figure 2B) until all of the sites have been converted to the corresponding, oxidized, -Fc$^+$ form (Figure 2C). This electrochemical process could be driven using any of a variety of electrochemical methods. We will consider the case of cyclic voltammetry (**Chapter ??**) since this is the most popular electrochemical method in use today.

A hypothetical cyclic voltammogram for the surface-confined redox reaction is shown in Figure 2. On the forward (positive-going) scan, an anodic wave is observed; this wave is associated with oxidation of the -Fc groups (Figure 1). This wave raises to a peak and then decays to zero current at potentials positive of the peak. This points out the first difference between a surface-confined redox reaction and a redox reaction in which the electroactive species is dissolved in solution. If the ferrocene were dissolved in the electrolyte solution (i.e. free Fc), the anodic current would gradually decrease at potentials positive of the peak (see **Chapter ??**). This gradual tailing of the current results because diffusion continuously brings fresh Fc to the electrode surface from the bulk solution. In the surface-confined case, there is no free Fc in the solution phase; therefore, once the -Fc has been completely oxidized, the current goes to zero. Finally, when the potential scan is reversed, a cathodic peak is observed; this peak is associated with the reduction of the -Fc$^+$ generated on the forward scan.

B. Electrochemistry at a "Multilayer" Film-Coated Electrode. Assume that a disk-shaped electrode (gold, platinum, carbon, etc.) has been coated with a film of poly(vinylferrocene) (Table II). This can be accomplished by dissolving the polymer in chloroform, applying a drop of the solution to the electrode surface, and allowing the solvent to evaporate. The electrochemistry of the resulting polymer film-coated electrode can be investigated using the

same electrochemical cell and equipment as described in our previous example.

The key feature of this polymer-film coated electrode is that it will always be thicker than the monolayer film consider in our previous example. Indeed, the film thickness can be controlled, at will, by varying the volume of solution applied and/or the concentration of polymer in the solution. The film thickness could be anywhere from tens of angstroms to hundreds of microns, or even thicker. This "multilayer film" situation is illustrated schematically in Figure 3A. Note that like the previous case, there are Fc groups sitting essentially right on the electrode surface. However, unlike the previous case, there are also Fc groups at distances removed from the electrode. The key questions that arise are - Can the Fc groups that are at distances quite removed from the electrode surface become electrochemically oxidized (Equation 3) and if so, by what mechanism does this oxidation occur?

The answer to the first question is yes - such multilayer films can be electrochemically oxidized and reduced using simple electrochemical experiments such as cyclic voltammetry. One mechanism by which such an oxidation process could occur is called "electron hopping." This mechanism was first proposed by Kaufman and Engler (36) and is illustrated schematically in Figure 3. Figure 3A shows the distribution of Fc sites in the polymer film before the electrochemical oxidation process is initiated. In Figure 3B the oxidation process has been initiated through appropriate control of the working electrode potential. Note that in complete analogy to the monolayer film case (Figure 1), the first thing that happens is that the Fc sites sitting directly on the electrode surface become oxidized. This produces a layer of Fc^+ sites immediately adjacent to the electrode surface (Figure 3B).

Initially all of the Fc sites further removed from the electrode surface are still in the

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unoxidized, Fc, state. Electrons can, however, "hop" from these distant Fc sites to the Fc^+ sites at the electrode surface (Figure 3C). Electron hopping occurs via a well-known chemical process called "electron self-exchange" whereby the reduced half of a redox couple (Fc) simply gives its electron to an oxidized counterpart (Fc^+). This reaction can be written as

$$Fc_1^+ \; + \; Fc_2 \; \relbar\relbar\relbar\!\!> \;\; Fc_1 \; + \; Fc_2^+ \qquad (8)$$

where the subscripts "1" and "2" are provided to show that the ferrocene molecule that was initially oxidized (subscript 1) ends up getting reduced and the ferrocene molecule that was initially reduced (subscript 2) ends up getting oxidized.

As shown in Figure 3C, the result of this first electron hop is that a layer of reduced, Fc, sites is regenerated at the electrode surface. What will happen to these Fc sites? Clearly, they will give up their electrons to the electrode regenerating a layer of Fc^+ at the electrode surface (Figure 3D). Note the net result is that we now have two layers of Fc^+ sites near the electrode but a whole lot of Fc sites still in the bulk of the polymer film. What happens next? Two more electron hops and another electron transfer will occur to yield three layers of Fc^+ sites at the electrode surface (Figure 3E). If we repeat this electron-hop/electron-transfer process many times, we will ultimately end up with a completely oxidized film (Figure 3F).

The above discussion shows that a multilayer polymer film can be electrochemically oxidized or reduced via this process called electron hopping. There is a feature of this process, however, that we have not yet considered. In Figure 3 we show that every time an electron leaves an Fc to create an Fc^+ in the polymer film, an anion must simultaneously come into the film from the contacting electrolyte solution. This co-transport of anions occurs because all phases (e.g. the polymer film) have the desire to remain electrically neutral. (This is called the

"electroneutrality principle." Lightning is a good example of the consequences of violating this basic principle.) Hence, when an Fc^+ is created in the film (by electron transfer to the electrode), an anion must also enter the film to insure that the film remains electrically neutral (Figure 3). Incidentally, you may be wondering how the contacting electrolyte-solution phase remains electrically neutral if anions are lost to the polymer-film phase. To answer this question, consider what is happening at the counter electrode in the solution phase (Chapter ??).

Electron hopping is not the only mechanism by which a multilayer film containing an electroactive species can be electrochemically oxidized or reduced. Consider an electrode surface that has been coated with a film of the cation exchange polymer Nafion (Table II). Let us assume that the electroactive cation Fe^{3+} has been ion-exchanged into this Nafion film (e.g. Equation 4). In principle, the Fe^{3+} in this film can be reduced via the following redox reaction.

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad (9)$$
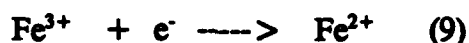
How will the Fe^{3+} groups at sites distant from the electrode surface be reduced in this film?

It is important to point out that the ion exchange polymer Nafion is fundamentally different from poly(vinylferrocene). In poly(vinylferrocene) the electroactive Fc groups are *covalently attached* to the polymer chain and therefore cannot move through the polymer film (either by diffusion or migration, see Chapter ??). The electroactive groups in this polymer are "nailed down." In contrast, the Fe^{3+} sites in the ion exchange polymer are not covalently bound. Hence, they can, in principle, move through the polymer film in the same way that the charge-balancing anions moved through the poly(vinylferrocene) film in Figure 3. Hence, the the Fe^{3+}'s in the portions of the Nafion film removed from the electrode surface could simply diffuse through the film to the electrode surface where the reduction to Fe^{2+} (Equation 9) would

occur. This would make the electrochemical reduction of the Fe^{3+} at the Nafion film-coated electrode completely analogous to the reduction of a solution of Fe^{3+} at an uncoated electrode.

So, we have two possibilities for the case of the ion exchange polymer film-coated electrode - reduction could occur by physical diffusion of the Fe^{3+} through the film, or reduction could occur via electron hopping through the film. How can we know which process is operative? Electrochemists have devoted a considerable amount of research effort to answering this question. The answer clearly depends on the nature of the polymer, the extent of swelling of the polymer by solvent, the size of the electroactive counterion, and the rate of the relevant electron self-exchange reaction (Equation 8). A simple-minded (first-order) answer to this question is as follows: If the magnitude of the diffusion coefficient for the electroactive ion in the polymer film is large and if the rate of the self-exchange reaction is low, physical diffusion will predominate. In contrast, if the diffusion coefficient for the electroactive ion is small and the self-exchange rate is high, electron hopping will predominate.

IV. CHARACTERIZATION AN ANALYSIS OF CHEMICALLY-MODIFIED ELECTRODES.

We begin with the most routine characterizations methods - electrochemical methods. We then discuss various instrumental methods of analysis. Such instrumental methods can be divided into two groups - *ex situ* methods and *in situ* methods. *In situ* means that the film on the electrode surface can be analyzed while the film is emersed in an electrolyte solution and while electrochemical reactions are occurring on/in the film. *Ex situ* means that the film-coated electrode must be removed from the electrolyte solution before the analysis. This is because most *ex situ* methods are ultra-high vacuum techniques. Examples include X-ray photoelectron spectroscopy (37), secondary-ion mass spectrometry (38, 39), and scanning or transmission

electron microscopies (40). Because *ex situ* methods are now part of the classical electrochemical literature, we review only *in situ* methods here.

A. Electrochemical Methods. The first question an electrochemist might ask about a chemically-modified electrode is - how much electroactive species is present in the film on the electrode surface? Cyclic voltammetry (see **Chapter ??**) can provide an answer to this question.

Let us begin by considering the self-assembled monolayer film discussed in the previous section. We define the amount of electroactive, surface-confined -Fc in this film as Γ_{Fc} which has units of moles of -Fc confined per cm^2 of gold electrode area. Γ_{Fc} can be determined from the voltammogram shown in Figure 2. The x-axis in this voltammogram is potential; however, since the potential is scanned at a constant rate (ν volts per second), any voltage, V, along the x-axis can be converted to a corresponding time, t, via t = V/ν. Hence, the x-axis can be easily converted to a time axis. Since, the y-axis is current, this would make the area under the forward, anodic, peak the charge corresponding to the oxidation of the surface-confined -Fc. Let's call this charge or area Q_{Fc}. Q_{Fc} can be easily obtained by electronic integration (which is available on many modern potentiostats) or by cutting the voltammogram from the paper it is recorded on and weighing. Γ_{Fc} can then be calculated from Q_{Fc} via Faraday's law,

$$\Gamma_{Fc} = Q_{Fc}/nFA \qquad (10)$$

where F is Faraday's constant and A is the electrode area.

There is one caveat that should be mentioned. Note that both the anodic and cathodic peaks in Figure 2 sit on top of flat (ideally) background currents. These are the capacitive currents associated with double charging (see **Chapter ??**). We do not want to include these capacitive currents in our determination of Γ_{Fc}. We want to integrate only the current associated with the oxidation of Fc, i.e. the "faradaic" current. We have delineated the area of the curve

associated with the faradaic current by extrapolating the background current (dashed line underneath the peak). The area we will use to determine Γ_{Fc} is the area under the peak but above this dashed line.

The voltammogram shown in Figure 2 is for the "reversible" or "Nernstian" case. As discussed in **Chapter ??**, this means that, at the scan rate employed, the rate of electron transfer is sufficiently high that the surface concentrations of -Fc and -Fc$^+$ are always at equilibrium with the applied electrode potential. For a surface-bound redox couple, the Nernstian case is characterized by a difference in potentials between the anodic and cathodic peaks (ΔE_{pk}) of zero volts; i.e. the cathodic wave sits right on top of the cathodic wave (Figure 2). It is worth mentioning that the formal potential (see **Chapter ??**) for the Nernstian case is simply the potential of the anodic and cathodic peak.

If the rate of electron transfer is low (or the scan rate is too high), electron transfer will not be able to adjust the surface concentrations of -Fc and -Fc$^+$ to values that are at equilibrium with the applied potential (quasi-reversible or totally-irreversible case, see **Chapter ??**). In this case, the anodic peak and the cathodic peaks will not be at the same potential; i.e. ΔE_{pk} will be greater than zero volts. Kinetic information about the surface-bound redox couple can be obtained from such quasireversible or irreversible voltammograms. For example, methods for obtaining the standard heterogeneous rate constant (see **Chapter ??**) for the surface-confined redox couple have been developed (41,42).

Let us turn our attention now to a multilayer film-coated electrode. What information can electrochemical experiments provide about such multilayer films? First, we can again obtain the quantity of electroactive sites in the polymer film; however, whether this can be done using

the simple voltammetric method, outlined above, depends on the film thickness and on the rate of charge transport in the film. If the multilayer film is thin and/or if the rate of charge transport is high, it may be possible to oxidized or reduce (i.e. electrolyze) all of the electroactive sites in the multilayer film during the voltammetric scan. If so, in analogy to Figure 2, the current at potentials beyond the voltammetric peaks will decay rapidly to zero. If this condition is satisfied, the quantity of electroactive sites in the film can be obtained from the areas under the peaks as per the monolayer film.

On the other hand, if the film is thick and/or if the rate of charge transport is low, only a fraction of the electroactive sites in the film will become electrolyzed during the voltammetric scan. The simplest way to think about this case is that the diffusion layer created at the electrode surface during the voltammetric scan (see **Chapter ??**) extends only a fraction of the way into the film. If this is the case, the voltammetric currents at potentials beyond the peaks will show gradual diffusional tails exactly like those observed in a cyclic voltammogram for a redox active molecule dissolved in a solution (see **Chapter ??**). The total quantity of electroactive sites in the film cannot be obtained from such voltammograms because only a fraction of the sites are electrolyzed during the scan. The total quantity of electroactive sites in such films can, however, be obtained using a simple coulometric method (43).

Scan rate clearly plays a role in determining whether all of the electroactive sites in the film are electrolyzed during the voltammetric scan. If the scan rate is very low (e.g. 1 mV s^{-1}), then it might be possible to electrolyze the entire film during the scan, in which case, a monolayer-type voltammogram (Figure 2) would be obtained. In contrast, if the scan rate is high (e.g. 10 V s^{-1}), it is more likely that only those sites in close proximity to the electrode

surface will be electrolyzed and a diffusional-type voltammogram will be obtained. In fact, it is often possible, through variation of the scan rate, to observe both monolayer-type (low scan rates) and diffusional-type (high scan rates) voltammograms for the same film.

A simple criterion has been developed for predicting when a monolayer-type and when a diffusional-type voltammogram might be observed (1). Let us assume that the thickness of the polymer film in question is d cm and that the "apparent diffusion coefficient" associated with charge transport in this film is D_{app} cm^2/ s^{-1}; the apparent diffusion coefficient (see below) is a measure of the rate of charge transport in the electroactive polymer film. We can define the "time constant" for electrolysis of the film as d^2/D. (Note that d^2/D has units of seconds). We can define a time scale parameter for the voltammetric scan as $RT/nF\nu$, where R is the gas constant, T is the temperature in degrees Kelvin, n is the number of moles of electrons transferred per mole of redox active sites, F is the Faraday constant, and ν is the scan rate in volts s^{-1}. (Note that $RT/nF\nu$ also has units of seconds.) If $Rt/nF\nu << d^2/D$ than only a fraction of the redox active sites in the film will be electrolyzed and the voltammetric wave will appear diffusional in nature. In contrast, if $Rt/nF\nu >> d^2/D$, then the entire film will be electrolyzed during the scan and a monolayer-type voltammogram will be obtained.

What is this parameter called the apparent diffusion coefficient, D_{app}? As indicated, above it is a measure of the rate of charge transport in a multilayer film at an electrode surface. What D_{app} *physically* means depends on the type of film being investigated. If the electroactive species is free to diffuse through the multilayer film, and if this diffusional process controls the rate of charge-transport, then D_{app} is just the diffusion coefficient for the redox active species in the polymer. Hence, in this case, D_{app} is completely analogous to the diffusion coefficient for an electroactive molecule dissolved in a solution (see Chapter ??). In contrast, if charge-

transport in the film occurs by electron hopping, then D_{app} is related to the rate of this electron hopping process. Electrochemists have measured D_{app} values for all types of films on electrode surfaces. A variety of electrochemical methods have been used including chronoamperometry (**Chapter ??**), chronocoulometry (**Chapter ??**), rotating disk voltammetry (**Chapter ??**), microelectrode voltammetry (**Chapter ??**), and AC impedance methods (**Chapter ??**).

Finally, it is worth commenting on the shape of the voltammetric wave obtained for a multilayer film on an electrode surface. If the rate of electron transfer is high (Nernstian case), the film voltammogram should be completely analogous to a voltammogram for a redox species dissolved in solution, e.g. diffusional anodic and cathodic peaks with $\Delta E_{pk} = 58/n$ mV (see **Chapter ??**). Such ideal waves are rarely observed for multilayer film-coated electrodes. For example, ΔE_{pk} values in excess of 58/n mVs are almost always observed. This could be caused by film resistance or slow heterogeneous kinetics (see **Chapter ??**). Alternatively, it is possible that the film is chemically heterogeneous and, as a result, the local chemical environments "seen" by the electroactive species in the film are not the same. Digital simulations (see **Chapter ??**) have been useful in exploring these contributions to non-Nernstian behavior in multilayer films on electrode surfaces (43).

B. <u>Methods Based on Optical Spectroscopy</u>. The electrochemical behavior of a modified electrode ultimately depends on structural details at the molecular level. For example, the molecular-level interaction between the redox site in the film and the solvent from the contacting solution phase might play an important role in the electrochemical response. Molecular-level details are often difficult to infer from electrochemical methods alone, but do avail themselves to spectroscopic analyses. In recent years there has been an explosion of new spectroscopic

techniques for characterizing modified electrodes and the electrode/solution interface, in general (44,45). In this section, we review some of these "spectroelectrochemical" methods.

1. <u>UV/Visible Transmission and Reflection Spectroscopy.</u> The simplest spectroscopic experiments are based on measurements of the amount of light transmitted by a sample. Such transmission-mode experiments are possible with chemically-modified electrodes if the substrate electrode is transparent. In fact, tin oxide or indium tin oxide ("ITO") electrodes are quite transparent over the entire visible spectrum (46). If the modifying layer contains visible-range chromophores, then examining potential-induced chemical changes in the film should be straightforward. For example, Elliott and Redepenning (47) coated a tin oxide electrode with a polymer that contained electroactive metal complex sites (Figure 4A). The ruthenium complexes have seven oxidation states, ranging from +2 to -4. After establishing the potentials at which the oxidation states change (via cyclic voltammetry) these authors collected visible absorption spectra as a function of applied potential. Typical data are shown in Figure 4B.

Unfortunately, most electrode materials are not transparent, and it is therefore necessary to employ reflectance methods. The reflectance, R, is defined as the ratio of the intensity of reflected light to that of the incident light. If there are absorbing chromophores at the reflecting surface, then R will be attenuated. Reflectance data are typically precessed by ratioing the measured reflectance, R, to the reflectance of some conveniently-defined standard, R_o. R_o might be the reflectance of a particular reference sample; e.g. the uncoated electrode. Alternatively, R_o might be the reflectance at the coated electrode at some reference potential, E_{ref} (48). In either case, a reflectance spectrum (analogous to an absorption spectrum) can be constructed by plotting $log(R/Ro)$ vs. wavelength or energy. Alternatively, the differential reflectance $\Delta R/R$

= $(R - R_o)/R_o$ can be plotted on the y-axis (48).

Reflectance experiments are generally more complicated than transmittance-mode experiments. This is because the reflected intensity depends not only on the identity and concentration of chromophores in the film, but on the angles of incidence and polarization of the incident light (48). For example, light polarized with its electric field parallel to the reflecting surface is usually reflected more efficiently than light polarized perpendicular to the surface. Polarization is particularly important at metal electrodes; if a molecule's transition dipole is aligned parallel to the metal surface, then light polarized in the plane of the surface will be "blind" to that particular absorption mode. This occurs because the incident light induces an image field in the metal that interferes destructively at the surface. Figure 5 demonstrates this effect quite dramatically (50).

2. Infrared Reflectance Spectroscopy. Infrared spectroscopy can provide a great deal of information on molecular identity and orientation at the electrode surface (51-53). Molecular vibrational modes can also be sensitive to the presence of ionic species and variations in electrode potential (51,52). In-situ reflectance measurements in the infrared spectrum engender the same considerations of polarization and incident angles as in UV/Visible reflectance. However, since water and other solvents employed in electrochemistry are strong IR absorbers, there is the additional problem of reduced throughput. This problem is alleviated with thin layer spectroelectrochemical cells (53).

A recent example of the application of in situ FTIR reflectance spectroscopy to modified electrodes can be found in the work of Korzeniewski and her group (54) on Pt electrodes coated with films of the polymer polyaniline. Figure 6 shows the reflectance spectrum (in $\Delta R/R$ units)

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of a polyaniline film-coated electrode as a function of applied potential. As the film becomes more oxidized, the band at ca. 1320 cm^{-1} is shifted to higher energies, a result consistent with an increasing C-N bond strength upon oxidation (54). The interaction between the dopant anion and the polymer was also investigated in this study. For example, molecular anions such as ClO_4^- and SO_4^{2-} are IR active, and thus detectable in an FTIR reflectance experiment. Korzeniewski found that vibrational bands for anions within the polyaniline film were blue shifted relative to the same anions in the bulk solution. This was ascribed to an ionic interaction between the dopant anions and the polyaniline film (54).

3. <u>Raman Spectroscopy.</u> Raman spectroscopy can offer vibrational information that is complimentary to that obtained by IR. Furthermore, since the Raman spectrum reveals the "backbone" structure of a molecular entity (55), it is particularly useful in the examination of polymer film-modified electrodes. There are also some distinct advantages over *in situ* IR. For example, both the mid- and far infrared spectral regions can be accessed with the same instrumental set-up (in IR spectroscopy, these two regions typically require separate optics) (55). Secondly, solvent such as water and acetonitrile are weak Raman scatterers; thus the solvent medium does not optically obscure the electrode surface as it does in an *in situ* IR experiment.

While signal loss due to the solvent may be low, it is also true that the Raman signal from the modified electrode surface may be weak, particularly for monolayer films. Hence, many workers exploit the surface enhanced Raman scattering (SERS) effect (56-58). Small metal particles, or protrusions on a roughened metal substrate, can amplify the incident electric field and lead to strong electromagnetic enhancements in the Raman signal of molecules adsorbed on their surfaces (57,58); enhancements can range from three-to-six orders of

magnitude. For Raman experiments employing excitation wavelengths in the visible spectrum, electromagnetic SERS enhancements occur on a few metals such as Ag, Au and Cu (58).

The Raman scattering signal can also be enhanced if one chooses an excitation wavelength corresponding to an electronic transition of the molecule of interest. This resonance Raman effect can enhance the signal by two-to-six orders of magnitude (55). Hence, exploiting both the surface enhancement and the molecular resonance leads to extremely low detection limits (e.g., picomolar and below).

Figure 7 shows an example of surface enhanced resonance Raman (SERRS) of a modified electrode. Cotton and her group examined the dye Nile Blue A in solution, at a glassy carbon electrode, and at a roughened silver electrode (59). By integrating currents in cyclic voltammetric measurements (see above), they found that multilayer films (50 to 100 monolayers) of the dye formed on the glassy carbon electrode. In contrast, monolayer films formed at the roughened silver electrode. In spite of the vast difference in coverage, the Raman signal from the roughened silver electrode is comparable in magnitude.

4. **Ellipsometry.** We mentioned above that the intensity of reflected light depends strongly on the angles of incidence and polarization of the incident light. In fact, reflection can cause a change in polarization. For example, if the incident light is linearly polarized at some angle between 0 (⊥) and 90 (||) degrees, the reflected light may be *elliptically polarized* on account of the different degrees to which the ⊥ and || components are reflected. While UV/Visible and infrared reflectance methods probe only reflected intensities, ellipsometry is a technique that measures the precise polarization state of the reflected light. The key advantage of ellipsometry is that one can determine both the thickness and the optical constants of a film (60-64). A full

treatment of this method is beyond the scope of this chapter. However, the reader is directed to a recent review by Collins and Kim (60) and the classic text by Azzam and Bashara (61).

5. Non-Linear Optical Techniques. A general objective in any *in situ* spectroscopic technique is to maximize the signal that arises specifically from the electrode surface. Non-linear optical techniques such as second harmonic generation (SHG) and sum frequency generation (SFG) are of interest because they involve optical signals that *by definition* can only arise at the electrode/solution interface (65).

Materials that have a non-zero second order susceptibility will produce light at twice the incident frequency. The magnitude of this effect is small, and has been a practical consideration only since the advent of lasers. If the symmetry of a crystal or other medium is such that it has a center of inversion, no SHG effect will be observed. However, surfaces by their very nature break this inversion symmetry. Hence, an SHG signal may arise at the electrode/solution interface even though both bulk phases may be considered centrosymmetric (66). The magnitude of the SHG signal is sensitive to surface conditions (e.g. electrode potential, ionic or molecular absorption, etc.). Surface spectroscopy is also feasible since the SHG signal will be enhanced if either the incident frequency (ω) or SHG (2ω) corresponds to an electronic absorption of a surface species (66).

Most SHG studies involve incident energies in the visible or near infrared spectrum. Infrared SHG studies are hindered by the current lack of sufficiently sensitive IR detectors. However, the sum frequency generation technique (SFG) allows one to obtain surface-specific vibrational spectra. In SFG, two lasers are focused on the sample surface, one with a fixed frequency in the visible and one with a tunable range of IR frequencies. The sample surface

experiences the sum of these frequencies. When the frequency of the infrared component corresponds to a molecular vibrational mode, there is an increase in the total SHG signal, which is detected at the visible frequency (66). The application of such techniques to *in-situ* electrochemistry and modified electrodes is still in its infancy, but the outlook for nonlinear optical methods is certainly promising (66).

C. *In-situ X-Ray Methods*. X-ray diffraction (XRD) is a routine method for determining crystal lattice parameters and molecular structure. The application of XRD to modified electrodes has been limited, particularly for actual molecular structure determination. Firstly, such experiments presuppose a single crystal electrode substrate. Secondly, the small amount of sample present in a thin film on an electrode surface means that the scattered intensities will be restrictively low, at least for commonly available X-ray sources (67). However, if one is fortunate enough to have access to a synchrotron, such experiments are quite feasible. For details, the reader is directed to an excellent review by Toney and Melroy (68). On the other hand, powder diffraction experiments with Cu or Mo K_α anode sources are straightforward, and can yield lattice constant data in-situ. For example, Ikeshoji and Iwasaki measured lattice constants for Prussian Blue films (see above) on gold electrode surfaces (69).

A method that requires a synchrotron source but not single crystal electrodes is extended X-ray absorption fine structure (EXAFS). Since the synchrotron produces a continuum of X-ray energies, one can collect an absorption spectrum analogous to those obtained in UV or IR spectroscopy. However, since X-radiation corresponds to core level electronic transitions, the spectra are characterized by a sharp absorption "edge" rather than broad bands. At energies above the edge, oscillations in the absorbance occur because of backscattering of the ejected

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photoelectron off the nearest atom neighbors. The magnitude and period of the oscillations depend on the distance and identity of the nearest neighbors. By fitting the spectra to a model, it is possible to determine the distance and number of near neighbors (71). Abruña and his group have used in-situ EXAFS to examine platinum electrodes modified with polymers containing Ru(II) or Os(II) complex sites (70).

D. Scanning Tunneling and Atomic Force Microscopy. Scanning tunneling (STM) was invented a decade ago by Binnig and Rohrer (72), and was first applied to the solid/liquid interface by Sonnenfeld and Hansma in 1986 (73). Since then, there have been numerous applications of STM to in-situ electrochemical experiments (74-76). Because the STM method is based on tunneling currents between the surface and an extremely small probe tip, the sample must be reasonably conductive. Hence, STM is particularly suited to investigations of redox and conducting polymer-modified electrodes (76,77).

Atomic force microscopy (AFM) is one of many techniques that rely on a force interaction (e.g., electrostatic or magnetic) between the probe tip and the surface (78). AFM relies on the attraction or repulsion forces that operate at atomic dimensions. Like STM, AFM may be done in-situ, but offers an advantage in that the sample may be conducting or insulating. For example, Murray and his group used AFM to monitor the electrodeposition of poly(phenylene oxide) (79), and later to actually alter the polymer surface with the probe tip (Murray calls this "nanodozing") (80).

E. Quartz Crystal Microbalance. Since the original work of Sauerbrey nearly four decades ago (81), the quartz crystal microbalance (QCM) has been applied in various contexts for the detection of mass changes at the nanogram level. The heart of the QCM method is a specially

cut quartz crystal which oscillates at some resonant frequency when an alternating voltage is applied across its thickness. Adsorption of foreign material (i.e. atoms and molecules) on the surface of the crystal leads to minute but detectable changes in the resonant frequency. The change in frequency Δf is related to the change in mass Δm via the Sauerbrey equation, $\Delta m = \Delta f^2 C$, where C is a constant that contains the resonant frequency before mass addition, and the sheer modulus and density of the quartz crystal (82). The first application of the QCM to in-situ electrochemistry was made by Nomura and Iijima, who monitored silver deposition from micro- to nanomolar solutions of silver nitrate (83).

The electrochemical quartz crystal microbalance (EQCM) simply employs one of the two oscillator drive electrodes as the working electrode (82). EQCM is particularly suited to modified-electrode studies where oxidation or reduction of the film on the electrode surface causes ions to enter or leave the film (84,85). For example, Varineau and Buttry used EQCM to monitor mass changes in poly(vinylferrocene) films on gold during concurrent cyclic voltammetric scans (84). Figure 8 shows the simultaneous voltammetric and EQCM results. Upon oxidation, indicated by the anodic wave in Curve A, the frequency of the quartz substrate decreases (Curve B) . This indicates that counter anions (PF_6^-) are entering the film as the Fc sites are oxidized to Fc^+. When the film is reduced (reverse scan) the frequency increases to its original value indicating, as might be expected, that upon reduction the anions are expelled from the film.

V. APPLICATIONS OF CHEMICALLY-MODIFIED ELECTRODES.

After twenty years of research, practical devices based on chemically-modified electrodes are now finding their way into the commercial market place. We review several recent

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examples here. In addition, chemically-modified electrodes have always been used as tools in fundamental scientific investigations. We discuss one very recent example.

A. Chemical Sensors. A chemical sensor is a device that provides the concentration of a particular chemical species (called the analyte) in a sample solution. For example, your doctor might want to know the concentration of Na^+ in your blood or an environmental scientist might want to know the concentration of DDT in a sample of river water. We have used these two examples of where a sensor might be useful to illustrate an important point - most sample solutions of "real-world" interest are extremely complicated mixtures containing many different chemical components; your blood is a good example. The sensor must somehow recognize and act upon the analyte of interest and ignore all of the other chemical species in the sample solution. This is an extremely challenging problem.

One of the goals in the chemically-modified electrode research area has been to develop new types of electrochemical sensors. Several review articles have recently been published on this subject (86,87). Our intent is not to provide another review of this voluminous literature. Rather, we would like to introduce the reader to the concepts behind the use of chemically-modified electrodes as electrochemical sensors. As we will see, the key to developing new sensors, is building chemical selectivity into the film covering the electrode surface so that only the analyte of interest is detected by the substrate electrode.

We begin by pointing out that this concept of covering an electrode surface with a chemically-selective layer predates chemically-modified electrodes. For example, an electrode of this type, the Clark electrode for analysis of O_2, has been available commercially for ca. 30 years. The chemically-selective layer in this sensor is simply a teflon-type membrane. Such

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membranes will only transport small, nonpolar molecules. Since O_2 is such a molecule, it is transported to an internal electrolyte solution where it is electrochemically reduced. The resulting current is proportional to the concentration of O_2 in the contacting solution phase. Other small nonpolar molecules present in the solution phase (e.g. N_2) are not electroactive. Hence, this device is quite selective.

Research into chemically-modified electrodes has led to a number of new ways to build chemical selectivity into films that can be coated onto electrode surfaces. Perhaps the simplest example is the use of the polymer Nafion (see Table II) to make selective electrodes for basic research in neurophysiology (88). Starting with the pioneering investigations by Ralph Adams, electrochemists have become interested in the electrochemical detection of a class of amine-based neurotransmitters in living organism. The quintessential example of this class of neurotransmitters is the molecule dopamine which can be electrochemically oxidized via the following redox reaction:

$$HO-\langle ring \rangle-CH_2CH_2\overset{H}{\underset{H}{N}}{}^{\oplus}-H \longrightarrow O=\langle ring \rangle=O-CH_2CH_2\overset{H}{\underset{H}{N}}{}^{\oplus}-H + 2H^+ + 2e^-$$

$$\tag{11}$$
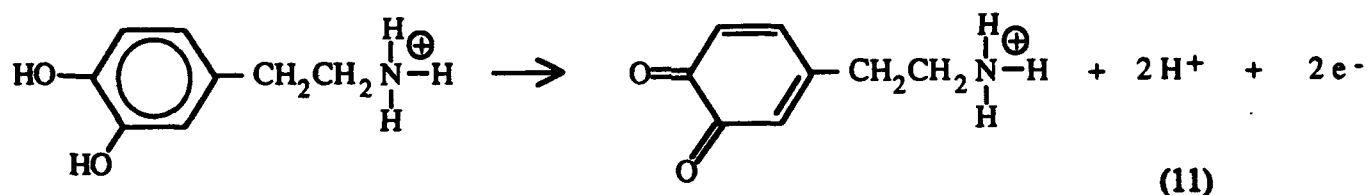
Electrochemists have shown that this molecule can be detected in the brains of living rats by surgically implanting electrodes into the rat's brain (88).

There is however, a major problem with this analysis. The cerebral fluid analyzed also contains relatively high concentrations of ascorbate. Ascorbate is oxidized at roughly the same potential as dopamine. Hence, ascorbate interferes with the determination of dopamine in the *in-vivo* electrochemical analysis. The solution to this problem - coating the surface of the

electrode to be implanted with a thin Nafion film - came out of a collaborative research effort between Martin's group and Adam's group (89). Note that at physiological pH values, dopamine is a cation and ascorbate is an anion. Because Nafion is a cation exchange polymer, it transports dopamine but rejects ascorbate. Hence, the Nafion-coated electrode provides the selectivity required for in vivo analysis of dopamine and other cationic neurotransmitters. The use of Nafion-coated electrodes has since become standard procedure for such investigations.

Nafion provides a very rudimentary form of chemical selectivity - selectivity based on the charge (cationic vs. anionic) of the analyte molecule. How can we build true molecule-recognition capability into a film that can be coated onto an electrode surface? One route that appears quite promising is to borrow from Mother Nature. Living systems have evolved a set of very selective chemical reagents called enzymes. An enzymes is a protein that recognizes and binds a specific molecule and then catalyzes some chemical transformation of that molecule. Because of this molecular-recognition capability, a variety of highly-successful enzymatic methods of chemical analysis have been developed (90). From the very inception of the chemically-modified electrode field, it seemed likely that enzymes could provide the molecule-recognition function that would lead to a new family of highly-selective electrochemical sensors. Electrochemists have been vigorously pursuing this goal for twenty years.

The enzyme-based sensor that has received the most attention is the glucose sensor based on glucose oxidase. Glucose oxidase catalyzes the two-electron, two-proton oxidation of glucose (GU) to gluconolactone (GL). The electron/proton acceptor is the cofactor flavin adenine dinucleotide (FAD). In living systems, the electrons and protons collected from glucose by FAD are passed on to O_2 to generate hydrogen peroxide. This chemistry can be represented as

follows:

$$GU \quad FAD \quad H_2O_2 \qquad\qquad (12)$$
$$GL \quad FADH_2 \quad O_2$$
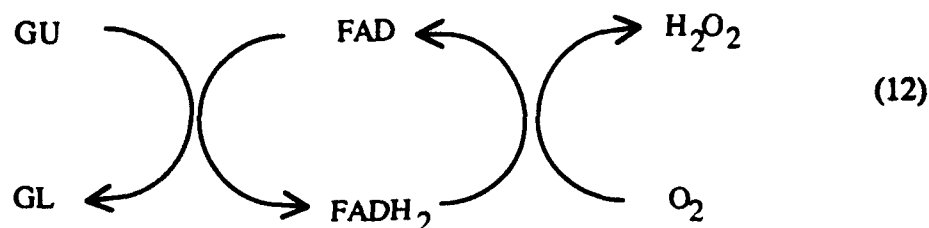
The most obvious way to incorporate this chemistry into an electrochemical sensor is to immobilize the enzyme onto an electrode surface and use this electrode to oxidize the hydrogen peroxide produced. An enzymatic sensor of this type was first prepared by Guilbault and Lubrano (91). Numerous variations on this theme have since appeared and sensors that employ this electrochemistry are now commercially available.

Detection of the enzymatic reaction (and, therefore, of glucose) via oxidation of H_2O_2 has some disadvantages. For example, a potential in excess of $+0.7$ V (vs. Ag/AgCl) must be applied to the substrate electrode in order to oxidize H_2O_2. If other oxidizable species are present in the sample (e.g. ascorbate, dopamine, etc.) these species will also be oxidized at this high positive potential. This creates the possibility for interference from these species. Hence, the molecular-recognition advantage of the enzyme will be lost. In 1984, Hill et al. proposed a simple solution to this problem (92). Instead of using O_2 as the electron acceptor (Equation 12), they employed an acceptor that could be re-oxidized at lower potentials. This allows the sensor to be operated at lower potentials and thus decreases the possibility of interference from oxidizable species in the analyte solution.

Derivatives of ferrocene are most often used as electron acceptors for glucose sensors of this type. In this case, the electron transfer reactions can be written as shown in Equation 13. Glucose sensors based on this electrochemistry are now commercially-available. Furthermore,

$$GU \quad FAD \quad Fc \qquad (13)$$
$$GL \quad FADH_2 \quad Fc^+$$
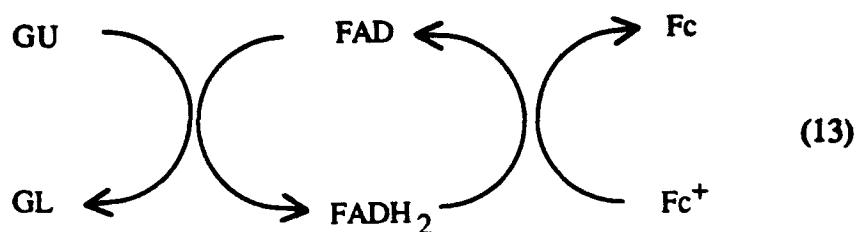
it seems likely that this concept will soon be expanded to other types of enzyme-based sensors. Hence, sensor development is proving to be one of the great success stories of the chemically-modified electrode research area.

B. Energy-Producing Devices. There are two primary types of electrochemical energy-producing devices - batteries and fuel cells. Both of these devices convert chemical energy into electrical energy via electrochemical reactions. The difference between a battery and a fuel cell is that a battery contains all of the chemicals required for the energy-producing reaction within the device package. Hence, the advantage of a battery is that it is a completely self-contained energy-producing device. In contrast, a fuel cell does not store its chemical reactants within the device itself. The reactants are supplied from external tanks. Hence, the advantage of the fuel cell is that it will run continuously as long as it is supplied with the appropriate chemical fuels. Fuel cells have been used extensively to provide electrical power for the U.S. space program.

The concepts of modified electrodes have contributed tremendously to battery and fuel cell development. For example, a schematic of an interesting new type of fuel cell, the polymer electrolyte fuel cell, is shown in Figure 9. Hydrogen gas is supplied to the anode and is oxidized via.

$$H_2 \longrightarrow 2 H^+ + 2 e^- \qquad (14)$$

Oxygen gas is supplied to the cathode and is reduced via.

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad (15)$$
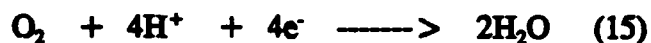
Note that hydronium ion is produced at the anode and consumed at the cathode. The purpose of the polymer membrane that separates these electrodes is to transport H^+ from the anode to the cathode. Hence, a cationically-conductive ion exchange polymer is used as the polymer electrolyte. The polymer Nafion, that has been discussed in so many other places in this chapter, is often used (see Table II).

The fuel cell in Figure 9 can conceptually be viewed as a combination of a *Nafion film-coated cathode* and a *Nafion film-coated anode*. Hence, the fuel cell is, in essence, a combination of two chemically-modified electrodes. This idea is, in fact, more than just a concept because electrochemical investigations of Nafion-film coated electrodes have been used to obtain fundamental chemical and electrochemical information that is relevant to the operation of such devices (93). For example, the kinetics of O_2 reduction in fuel cells can be investigated at such modified electrodes; the solubility and diffusion coefficient for O_2 in Nafion and the proton conductivity of this membrane material can also be determined. Chemically-modified electrodes have made analogous contributions to battery development.

C. <u>Electrochromic Devices</u>. In Section II D, above, we introduced the concept of electrochromism - the ability of a material to change color upon a change in its oxidation state. Electrochemists are interested in using electrochromism to make devices that change color on command. For example, let us assume that you are sitting in your car at the end of rain storm. During the storm, the sky was dark but now the clouds have cleared and it is extremely bright and sunny. Wouldn't it be nice if you could just turn a knob on your dash board and tint your windows a little so that the sun does not hurt your eyes or interfere with your driving? This is the concept behind the "smart window." A concept being vigorous-pursued by electrochemists

at various companies around the world.

A general schematic for a smart window is shown in Figure 10. This device is, quite literally, two chemically-modified electrodes sandwhiched together. In this case the films coating the electrode surfaces are electrochromic materials. A polymer electrolyte, analogous to that used in the fuel cell discussed above, is sandwiched between these two electrochromic material-coated electrodes. In a recent example of this concept by Habib and Maheswari of General Motors Research Laboratories (94), the cathodic electrochromic material was a tungsten oxide and the cathodic electrochromic material was the material prussian blue, discussed in Part II of this chapter. It seems likely that electrochromic cells will soon find their way into the commercial market place.

D. Fundamental Chemistry. In addition to leading to new types of electrochemical devices, modified electrodes have been used as tools in fundamental scientific investigations. The objective of such investiagtions is simply to obtain fundamental scientific information. A good example is the use of modified electrodes to study the fundamentals of electron transfer (ET) reactions. For example, Christopher Chidsey has used self assembled-monolayers (alkanethiols) with terminal ferrocene functions to probe ET processes at the electrode/solution interface (95). Because the electroactive sites are bound to the electrode, there is no need to separate kinetic and diffusional components of the measured current. Also, because the electrode potential can be varied, the driving force $\Delta G°$ for the reaction can be changed easily (in homogeneous ET you have to change one member of the donor/acceptor pair to change the driving force). Hence, Chidsey is able to quantitatively evaluate Marcus Theory (96) which postulates a quadratic relation between $\Delta G°$ and the activation Gibbs energy ΔG^*. Finally, the donor - acceptor

distance can be varied by simply changing the length of the alkane group (95).

VI. CONCLUSIONS.

Chemically-modified electrodes have been the dominant research theme in electrochemistry for two decades. As discussed in this chapter, many tangible benefits have accrued from this research effort. An important intangible benefit has also accrued. Through this research effort, electrochemists have raised the scientific profile of their research area and have helped break down barriers between traditional scientific disciplines. For example, because of research on chemically-modified electrodes, a polymer scientist might now use such a device to synthesize an interesting new material. An experimental physicist might then conduct exotic spectroscopic measurements on this material, and a theoretical physicist might try to calculate the band structure of this material. Or, because of this research effort, a physiologist might use a chemically modified electrode for in vivo investigations of a bioactive substance, or a medical doctor might use a modified-electrode sensor to help diagnose disease. Penetration of research ideas across traditional scientific boundaries is essential to modern science. The chemically-modified electrode research area is a good example of such a borderless research topic.

What about the future? The chemically modified electrode field is now quite mature. A large fraction of the necessary fundamental work had already been done. Hence, further development of commercial applications of modified-electrode technology must dominate future research efforts. Since such product-development research is applied in nature, much of this research should be done in the private sector and/or by chemical and electrochemical engineers. This is called technology transfer and is the logical step for this next, extremely important, phase

of the overall research effort. So our question to the current and future generations of fundamentally-oriented electrochemists is - Will another research topic ever galvanize our endeavors the way chemically-modified electrodes have? If so, what is it?

Acknowledgements

Literature Cited

1. I. Rubinstein in J. Mitchell, Jr., Ed. Applied Polymer Analysis and Characterization, Vol. II, Hanser, Munich, 1991.

2. A. Merz, in Topics in Current Chemistry, Vol 152, 1990, Springer-Verlag, Berlin, 1990.

3. E. Barendrecht, *J. Applied Electrochem.* 1990, 20, 175.

4. H.D. Abruna, *Coordination Chemistry Reviews*, 1988, 86, 135.

5. R.W. Murray, A.G. Ewing, and R.A. Durst, *Anal. Chem.*, 1987, 59, 379A.

6. C.E.D. Chidsey and R.W. Murray, *Science*, 1986, 231, 25.

7. L.R. Falukner, *Chemical and Engineering News*, Vol. 62 (9), February 27, 1984, p. 28.

8. W.J. Albery and A.R. Hillman, *Annual Reports on the Progress of Chemistry*, Section C, Physical Chemistry, Vol. 78, p. 377, 1981, The Royal Society of Chemistry, London.

9. A.W. Adamson, Textbook of Physical Chemistry, Academic Press, 1973, NY, pp. 664-670.

10. R.F. Lane and A.T. Hubbard, *J. Phys. Chem.*, 1973, 77, 1401.

11. R.F. Lane and A.T. Hubbard, *J. Phys. Chem.*, 1973, 77, 1411.

12. A.P. Brown and F.C. Anson, *Anal. Chem.*, 1977, 49, 1589.

13. L.H. Dubois and R.G. Muzzo, *Anal. Rev. Phys. Chem.*, 1992, 43, 437.

14. M.M. Walczak, C. Chung, S.M. Stole, C.A. Widrig, and M.D. Porter, *J. Am. Chem. Soc.*, 1991, 113, 2370.

15. R.W. Murray *Acc. Chem. Res.*, 1980, 13, 135.

16. D.C. Bookbinder and M.S. Wrighton, *J. Electrochem. Soc.*, 1983, 130, 1080.

17. B.F. Watkins, J.R. Behling, E. Kariv, and L.L. Miller, *J. Am. Chem. Soc.*, 1975, 97, 3549.

18. L. Netzer and J. Sagiv, *J. Am. Chem. Soc.*, 1983, 105, 674.

19. H. Lee, L.J. Kepley, H-G. Hong, and T.E. Mallouk, *J. Am. Chem. Soc.* 1988, 110, 618.

20. L.L. Miller and M.R. Van de Mark, *J. Am. Chem. Soc.*, 1978, 100, 3223.

21. A. Merz and A.J. Bard, *J. Am. Chem. Soc.*, 1978, 100, 3222.

22. N. Oyama and F.C. Anson, *J. Am. Chem. Soc.* 1979, 101, 739.

23. M.N. Szentirmay and C.R. Martin, *Anal. Chem.* 1984, 56, 1898.

24. C.R. Martin, T.A. Rhodes, and J.A. Ferguson, *Anal. Chem.*, 1982, 54, 1639.

25. C.R. Martin and L.S. Van Dyke in R.W. Murray, Ed. Molecular Design of Electrode Surfaces, John Wiley, NY, 1992.

26. A.F. Diaz and J. Bargon in T.A. Skotheim, Ed. Handbook of Conducting Polymers, Marcel Dekker, NY, 1986.

27. H.D. Abruña, P. Denisevich, M. Umana, T.J. Meyer, and R.W. Murray, *J. Am. Chem. Soc.*, 1981, 103, 1.

28. A. Fitch, *Clays and Clay Minerals*, 1990, 38, 391.

29. D.R. Rollison, *Chem. Rev.*, 1990, 90, 867.

30. K. Itaya, I. Uchida, and V.D. Neff, *Acc. Chem. Res.*, 1986, 19, 162.

31. Brown, *J. Philos. Trans.*, 1724, 33, 17.

32. C.A. Goss, C.J. Miller, and M. Majda, *J. Phys. Chem.*, 1991, 300, 377.

33. A. Despic and V. Parkhutik, in J. Bockris, R.E. White, and B.E. Conway, Eds. Modern Aspects of Electrochemistry, Plenum, NY, 1989, Ch. 6.

34. C.A. Foss, Jr., G.L. Hornyak, J.A. Stockert, and C.R. Martin, *Advanced Materials*, 1993, 5, 135.

35. J.S. Facci, *Tech. Chem.*, 1992, 22, 119.

36. F.B. Kaufman and E.M. Engler, *J. Am. Chem. Soc.*, 1979, 101, 549.

37. R. Kötz, in C. Gutiérrez and C. Melendres (Eds.), *Spectroscopic and Diffraction Techniques in Interfacial Electrochemistry*, Kluwer, Dordrecht, 1990.

38. F. Chao, J.L. Baudin, M. Costa, and P. Lang, *Makromol. Chem., Macromol. Symp.,* 1987, 8, 173.

39. P.C. Lacaze and G. Tourillon, *J. Chim. Phys., Phys.-Chim. Biol.,* 1979, 76, 371.

40. Y.-M. Tsou, H.-Y. Liu, and A.J. Bard, *J. Electrochem. Soc.,* 1988, 135, 1669.

41. A.T. Hubbard and F.C. Anson in A.J. Bard, Ed., Electroanalytical Chemistry, Vol. 4, Marcel Dekker, NY, 1970.

42. E. Laviron, *J. Electroanal. Chem.,* 1979, 101, 19.

43. C.R. Martin, I. Rubinstein, and A.J. Bard, *J. Am. Chem. Soc.,* 1982, 104, 4817.

44. H.D. Abruña (Ed.) Electrochemical Interfaces: Modern Techniques for in-situ Interface Characterization," VCH, New York, 1991.

45. C. Gutiérrez and C. Melendres (Eds.), Spectroscopic and Diffraction Techniques in Interfacial Electrochemistry, Kluwer, Dordrecht, 1990.

46. N. Winograd and T. Kuwana, *Electroanalytical Chem.,* 1974, 7, 1.

47. C.M. Elliott and J.G. Redepenning, *J. Electroanal. Chem.,* 1986, 197, 219.

48. W. Plieth, in ref. 45.

49. K. Ashley and S. Pons, *Trends in Analytical Chemistry,* 1986, 5, 263.

50. P.H. Schmidt and W.J. Plieth, *J. Electroanal. Chem.,* 1986, 201, 163.

51. K. Ashley, F. Weinert, M.G. Samant, H. Seki, and M.R. Philpott, *J. Phys. Chem.,* 1991, 95, 7409.

52. K. Ashley, F. Weinert and D.L. Feldheim, *Electrochimica Acta,* 1991, 36, 1863.

53. a) K. Ashley, *Spectroscopy,* 1990, 5, 22. b) A. Bewick, K. Kunimatsu and B.S. Pons, *Electrochimica Acta,* 1980, 25, 465. c) S. M. Stole, D.D. Popenoe, and M.D. Porter, in ref. 44.

54. D. Seeger, W. Kowalchyk, and C. Korzeniewski, *Langmuir,* 1990, 6, 1527.

55. H.H. Willard, L.L. Merritt, J.A. Dean and F.A. Settle, <u>Instrumental Methods of Analysis</u>, Wadsworth, Belmont, CA, 1988.

56. M. Fleischmann, P.J. Hendra, and A.J. McQuillan, *Chem. Phys. Lett.*, 1974, 26, 163.

57. R.K. Chang and T.E. Furtak, (Eds.) <u>Surface Enhanced Raman Spectroscopy</u>, Plenum, New York, 1982.

58. J.E. Pemberton, in ref. 44.

59. F. Ni, M. Feng, L. Gorton, and T.M. Cotton, *Langmuir*, 1990, 6, 66.

60. R.W. Collins and Y.- T. Kim, *Anal. Chem.*, 1990, 62, 887A.

61. R.M.A. Azzam and N.M. Bashara, <u>Ellipsometry and Polarized Light</u>, North Holland, Amsterdam, 1977.

62. J. O'M. Bockris, M.A.V. Devanathan, and A.K.N. Reddy, *J. Electroanal. Chem.*, 1963, 6, 61.

63. A. Redondo, E.A. Ticianelli, and S. Gottesfeld, *Mol. Cryst. Liq. Cryst.*, 1988, 160, 185.

64. Y.-T. Kim, R.W. Collins, K. Vedam, and D.L. Allara, *J. Electrochem. Soc.*, 1991, 138, 3266.

65. a) G.L. Richmond, in ref 44. b) Y. R. Shen, <u>Principles of Nonlinear Optics</u>, Wiley, New York, 1984.

66. Y.R. Shen, in ref. 45.

67. J. Robinson, in ref. 45.

68. M.F. Toney and O.R. Melroy, in ref. 44.

69. T. Ikeshoji and T. Iwasaki, *Inorg. Chem.*, 1988, 27, 1123.

70. M.J. Albarelli, J.H. White, G.M. Bommarito, M. McMillan and H.D. Abruña, *J. Electroanal. Chem.*, 1988, 248, 77.

71. H.D. Abruña, in ref. 44.

72. G. Binnig, H. Rohrer, and C. Gerber, *Phys. Rev. Lett.*, 1982, 49, 57.

73. R. Sonnenfeld and P.K. Hansma, *Science*, 1986, 232, 211.

74. K. Itaya, S. Sugawara, K. Sashikata and N. Furuya, *J. Vac. Sci. Technol. A*, 1990, 8, 515.

75. K. Uosaki and H. Kita, *J. Vac. Sci. Technol. A*, 1990, 8, 520.

76. F.F. Fan and A.J. Bard, *J. Electrochem. Soc.*, 1989, 136, 3216.

77. J.H. Schott, C.P. Araña, H.D. Abruña, H.H. Petach, C.M. Elliott, and H.S. White, *J. Phys. Chem.*, 1992, 96, 5222.

78. D. Sarid and V. Elings, *J. Vac. Sci. Technol. B*, 1991, 9, 431.

79. C.A. Goss, J.C. Brumfield, E.A. Irene, and R.W. Murray, *Langmuir*, 1992, 8, 1459.

80. J.C. Brumfield, C.A. Goss, E.A. Irene, and R.W. Murray, *Langmuir*, 1992, 8, 2810.

81. G. Sauerbrey, *Z. Phys.*, 1935, 155, 206.

82. S. Bruckenstein and M. Shay, *Electrochimica Acta*, 1985, 30, 1295.

83. T. Nomura and M. Iijima, *Anal. Chim. Acta*, 1981, 131.

84. P.T. Varineau and D.A. Buttry, *J. Phys. Chem.*, 1987, 91, 1292.

85. D.A. Buttry and M.D. Ward, *Chem. Rev.* 1992, 92, 1355.

86. P.W. Stoecker and A.M. Yacynych, *Selective Electrode Rev.*, 1990, 12, 137.

87. J. Wang, *Electroanal.* 1991, 3, 225.

88. G.A. Gerhardt, A.F. Oke, G. Nagy, B. Moghaddam, and R.N. Adams, *Brain Res.*, 1983, 290, 390.

89. G. Nagy, G.A. Gerhardt, A.F. Oke, M.E. Rice, R.N. Adams, R.B. Moore, III, M.N. Szentirmay, and C.R. Martin, 1985, 188, 85.

90. G.G. Guilbault, Enzymatic Methods of Analysis, Pergamon, NY, 1970.

91. G.G. Guilbault and G.L. Lubrano, *Anal. Chim. Acta*, 1973, 64, 439.

92. A.E.G. Cass, G. Davis, G.D. Francis, H.A.O. Hill, W.J. Aston, I.J. Higgins, E.V. Plotkin, L.D.L. Scott, A.P.F. Turner, *Anal. Chem.*, 1984, 56, 667.

93. A. Parthasarathy, S. Srinivasan, A.J. Appleby, and C.R. Martin, *J. Electrochem. Soc.*, 1992, 139, 2856.

94. M.A. Habib and S.P. Maheswari, *J. Electrochem. Soc.*, 1992, 139, 2155.

95. C.E.D. Chidsey, *Science*, 1991, 251, 919.

96. R.A. Marcus, *J. Chem. Phys.*, 1965, 43, 679.

Table I. Some representative electroactive molecules that have been chemisorbed onto electrode surfaces.
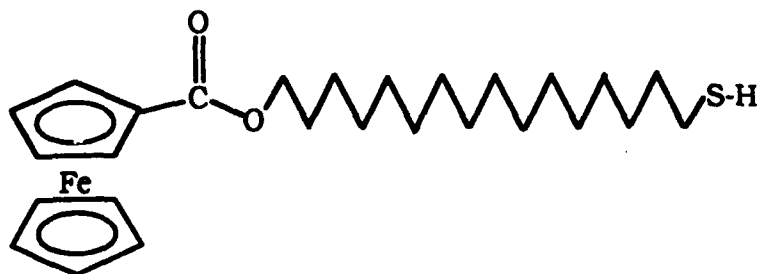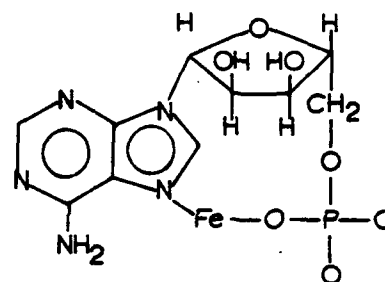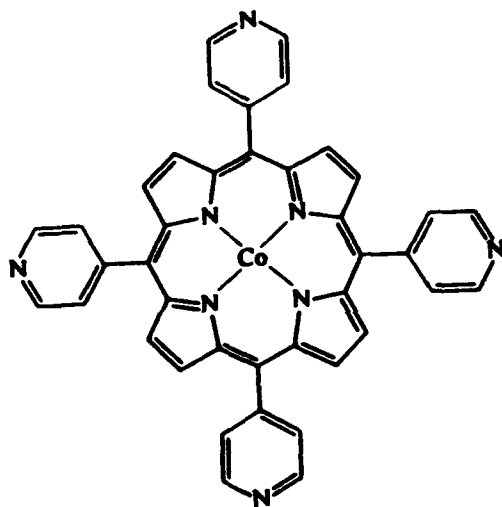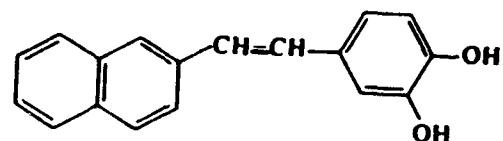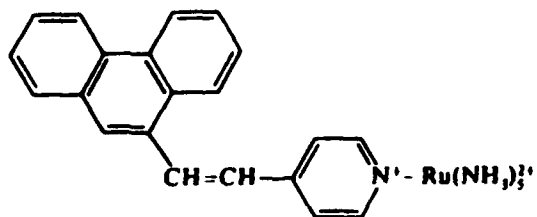
Table II. Some representative polymers that have been used to modify electrode surfaces
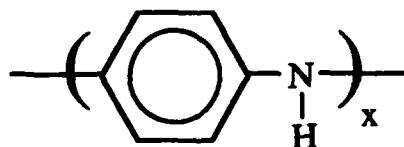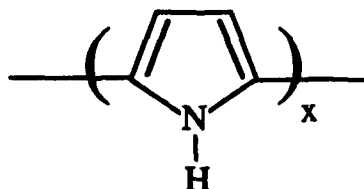
Redox Polymers

$$-(CH_2-CH)_x-$$

Fe

$$-(CH_2-CH)_x-$$

$$NO_2$$
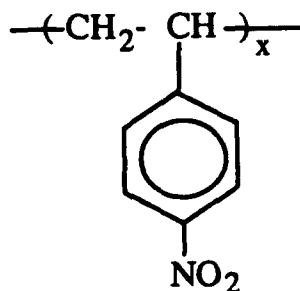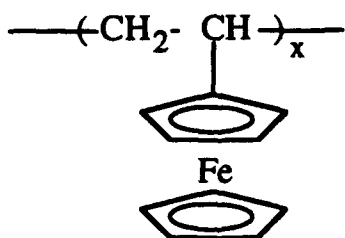
Ion Exchange and Coordinating Polymers

$$-[(CF_2-CF_2)_x-(CF-CF_2)_y-$$
$$O$$
$$CF_2$$
$$CF-CF_3$$
$$O-CF_2CF_2SO_3H$$

(Nafion)

$$-(CH_2-CH)_x-$$
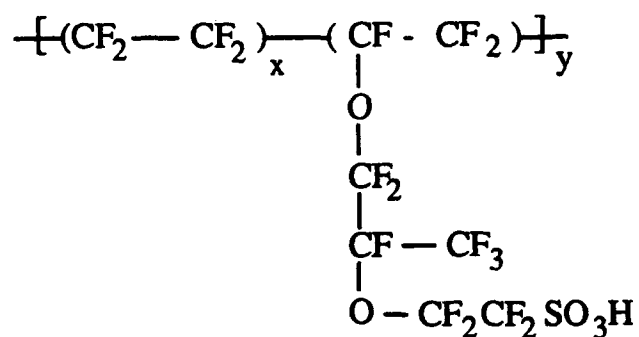
N

Electronically Conductive Polymers

$$-()_x-$$
N
H

$$-(-N)_x-$$
H
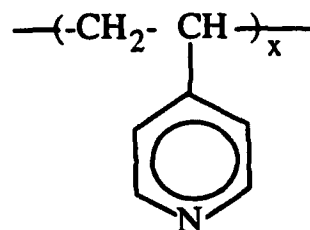
A.
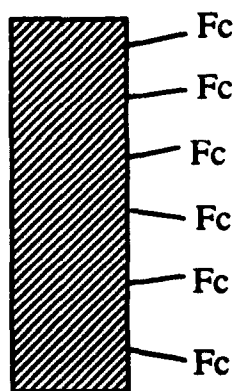
Electrode   Solution

B.
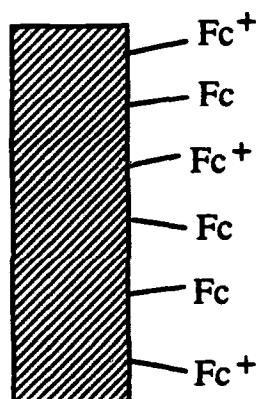
C.
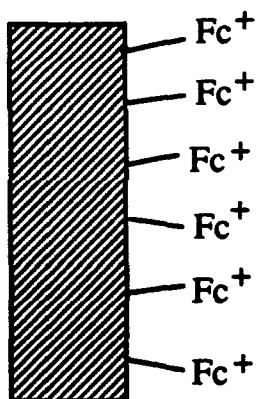
Figure 1.   Schematic diagram of the electrochemical oxidation of a monolayer of a surface-confined ferrocene (Fc) derivative. A. Before, B. During, C. After oxidation.
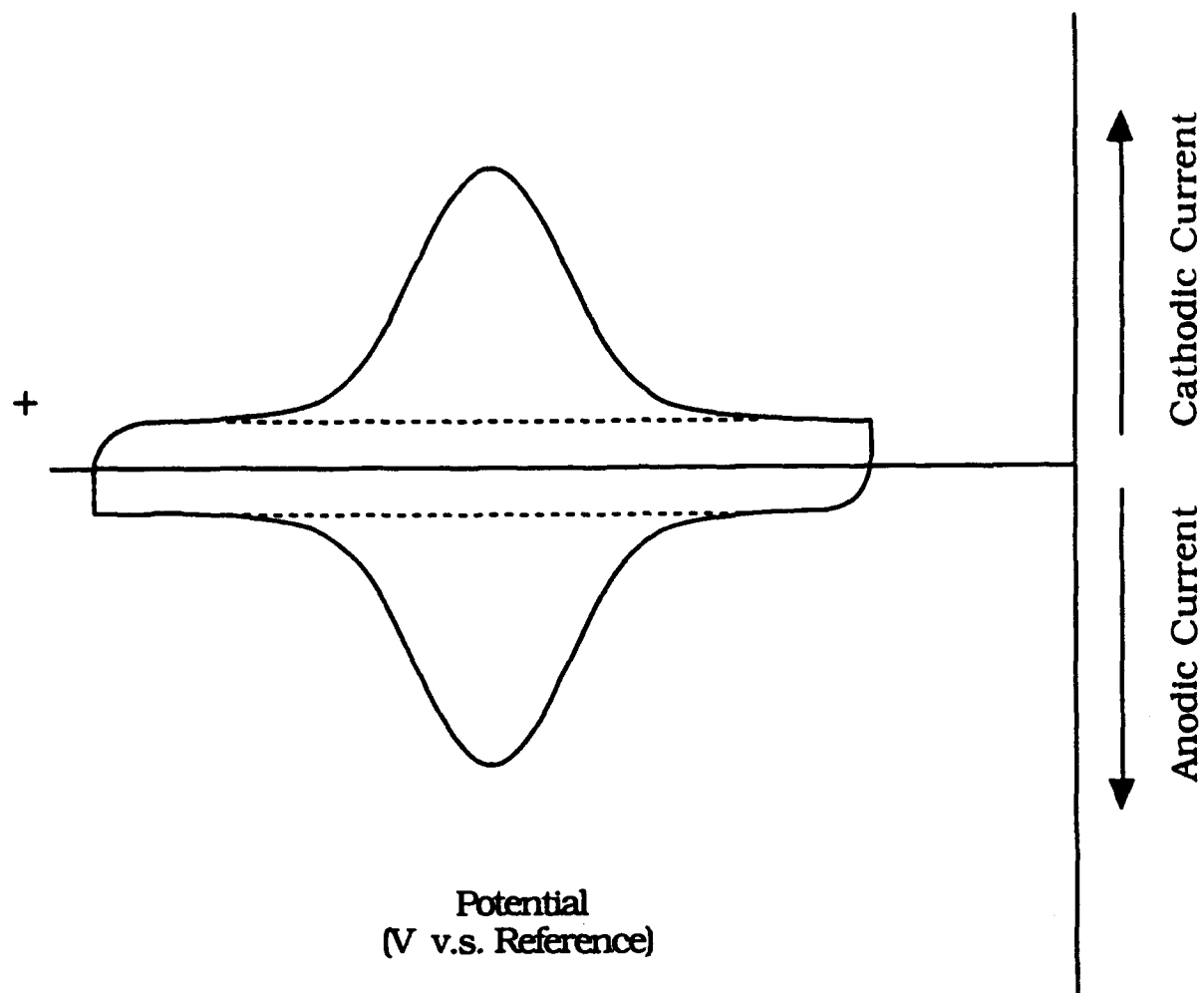
Figure 2. Hypothetical cyclic voltammogram for the surface oxidation process illustrated in Figure 1.
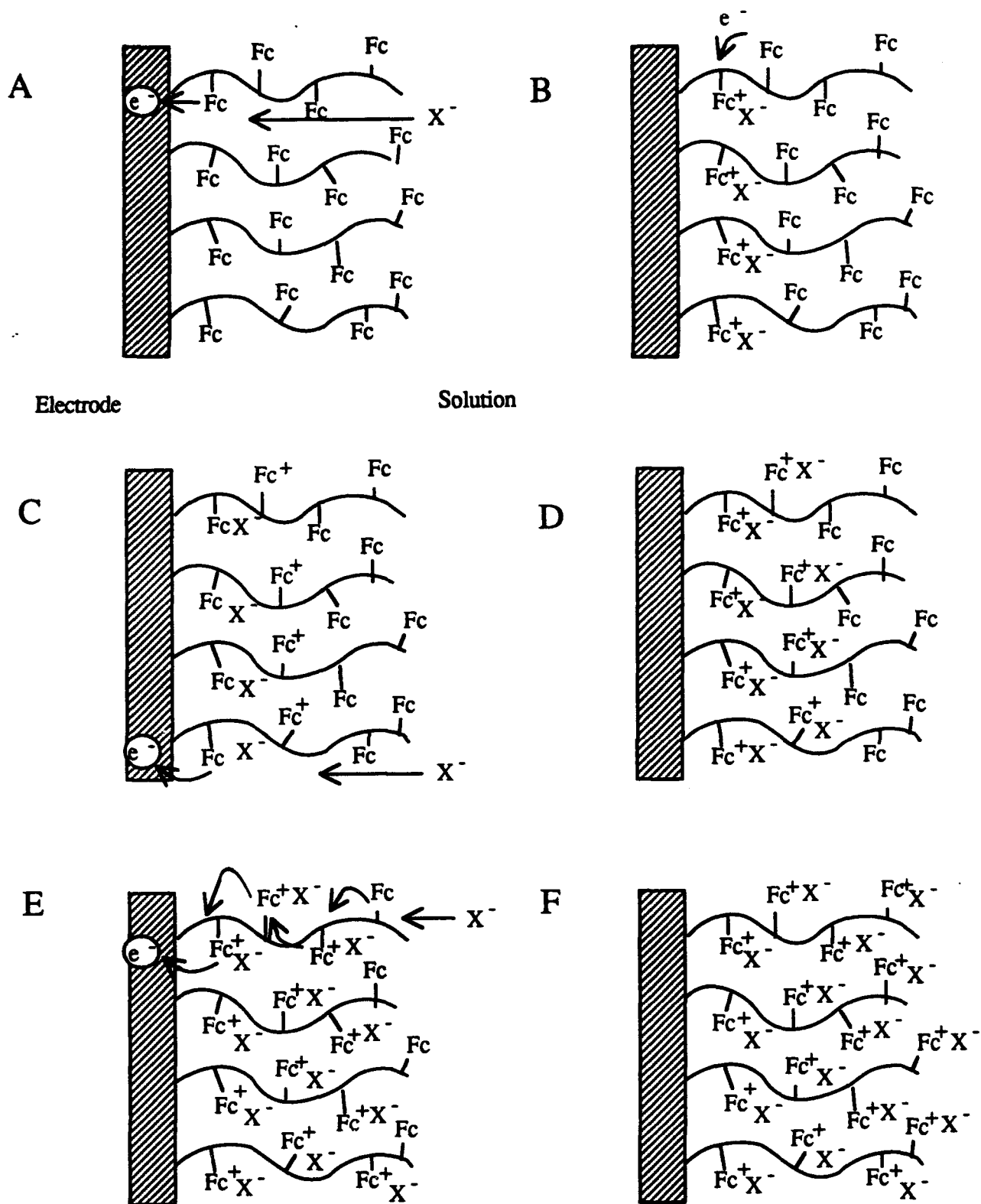
Figure 3. Schematic diagram of the electrochemical oxidation of a multi-layer film containing covalently - attached ferrocene (Fc) sites. X^- represents anions from the supporting electrolyte that neutralize the Fc^+ sites created. Figures 3A through 3F represent various times during the oxidation process.
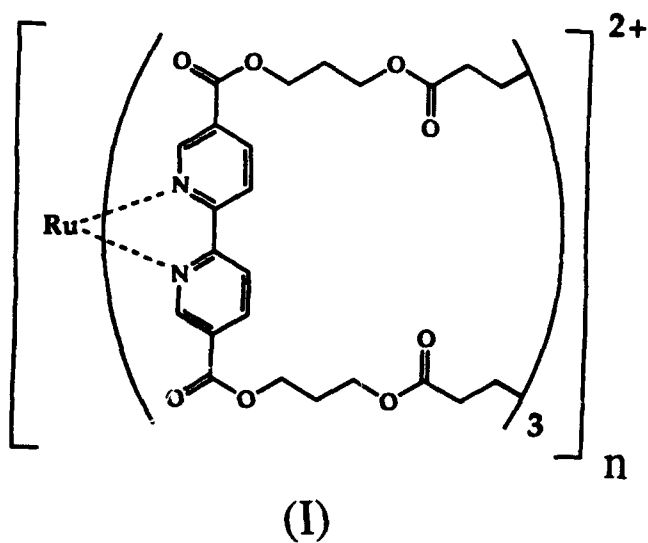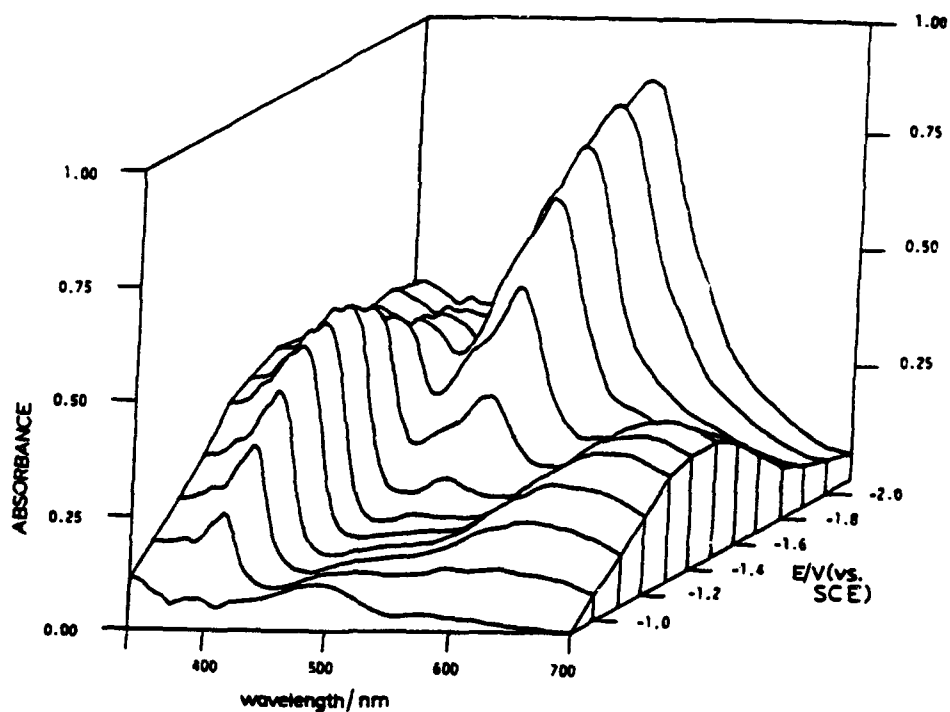
Figure 4 (A) Structure of poly - (Ru (II) tris - (5, 5' dicarbo(3-acrylatoprop- 1 - oxy)-2, 2' bipyridine)).
(B) UV/Vis spectra of (I) thermally polymerized on SnO_2 transparent electrode as a function of applied potential. Film thickness ca. 0.2 µm. Potential measured against Ag/Ag^+ (0.1 M). From reference 47
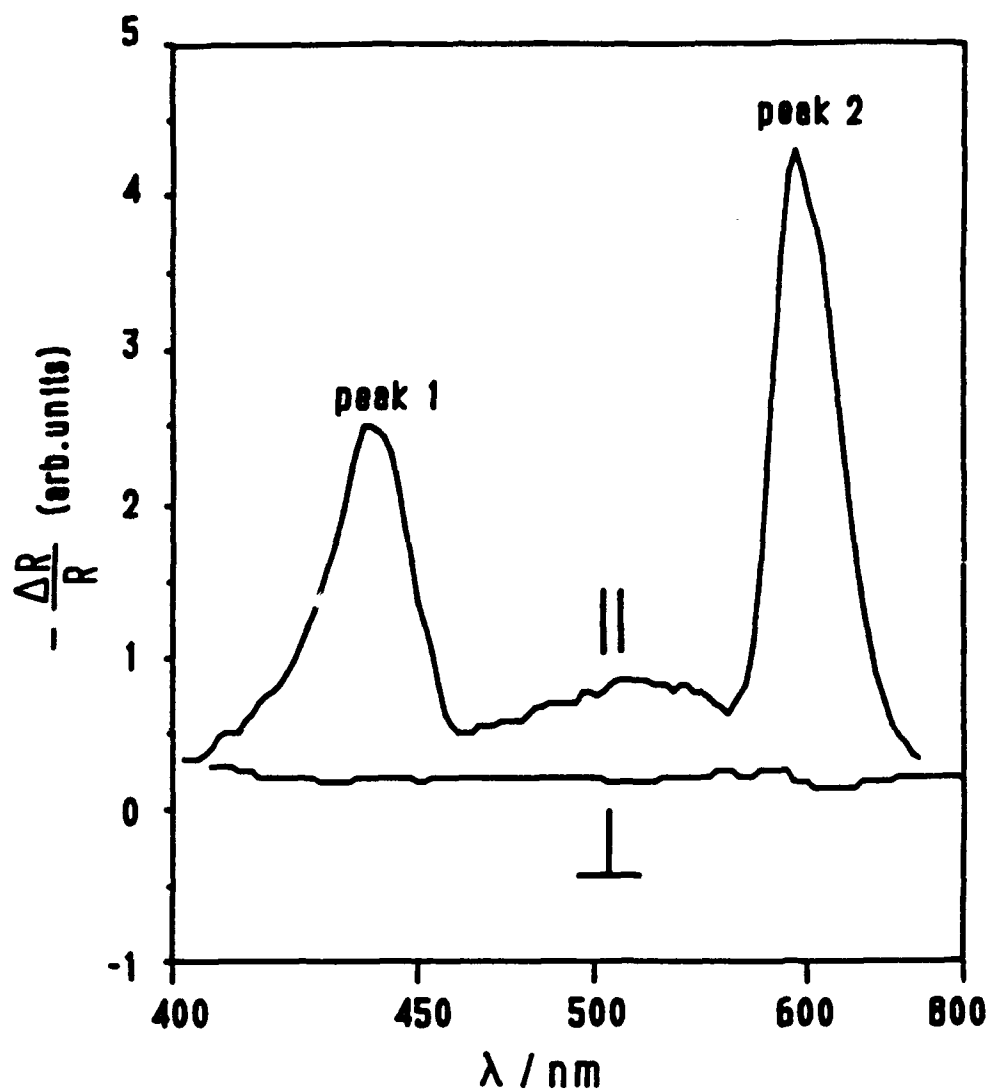
Figure 5 Potential modulated reflectance spectrum of p-aminonitrobenzene (PANB) on platinum (solution phase 0.5 M Na2SO4 + 0.05 mM PANB). Applied D.C. 0.44 V v.s. SHE. Modulation amplitude ± 50 mV. Modulation frequency 33 Hz. Incidence angle 65 °. "∥" signifies incident polarization parallel to incident plane and perpendicular to electrode surface. "⊥" signifies incident polarization perpendicular to incident plane (hence parallel to electrode surface). From reference 50.
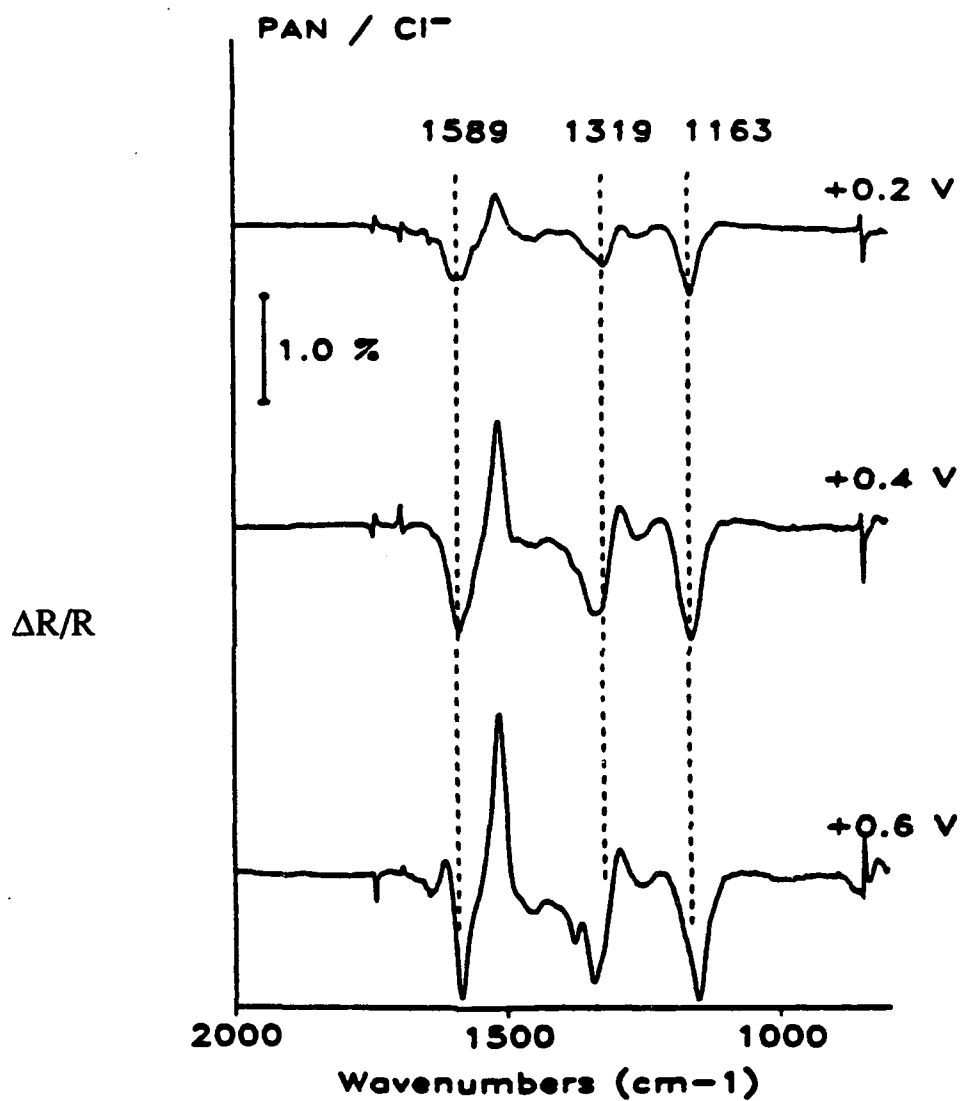
Figure 6 In situ infrared reflectance spectra of polyaniline modified electrodes in solution containing 0.10M HCl. Spectra collected at applied potentials indicated at right of curves, and normalized according to equation 12 using R_0 collected at -0.1V. Potentials measured against saturated calomel electrode. From reference 54.
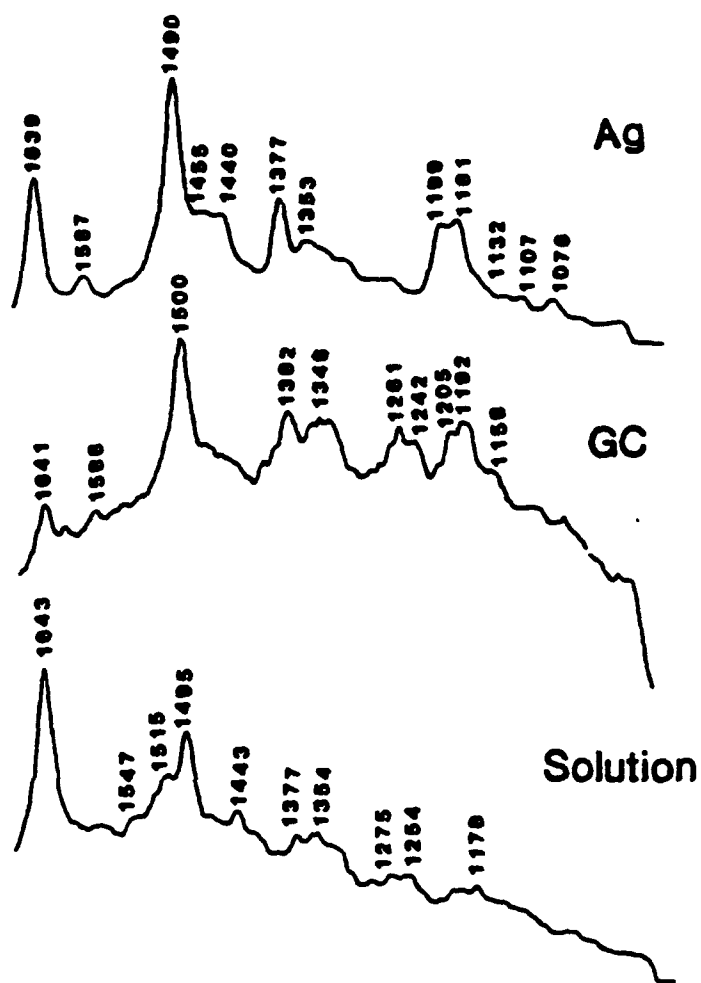
Figure 7 Raman spectra of Nile Blue A on roughened Ag electrode, glassy carbon electrode (GC), and in solution. Ph = 9.0. Excitation wavelength 488 nm. Laser power for Ag, 10 mW ; for GC, 200 mW; for solution 180 mW. Raman shifts in cm^{-1} shown above peaks. From reference 59.
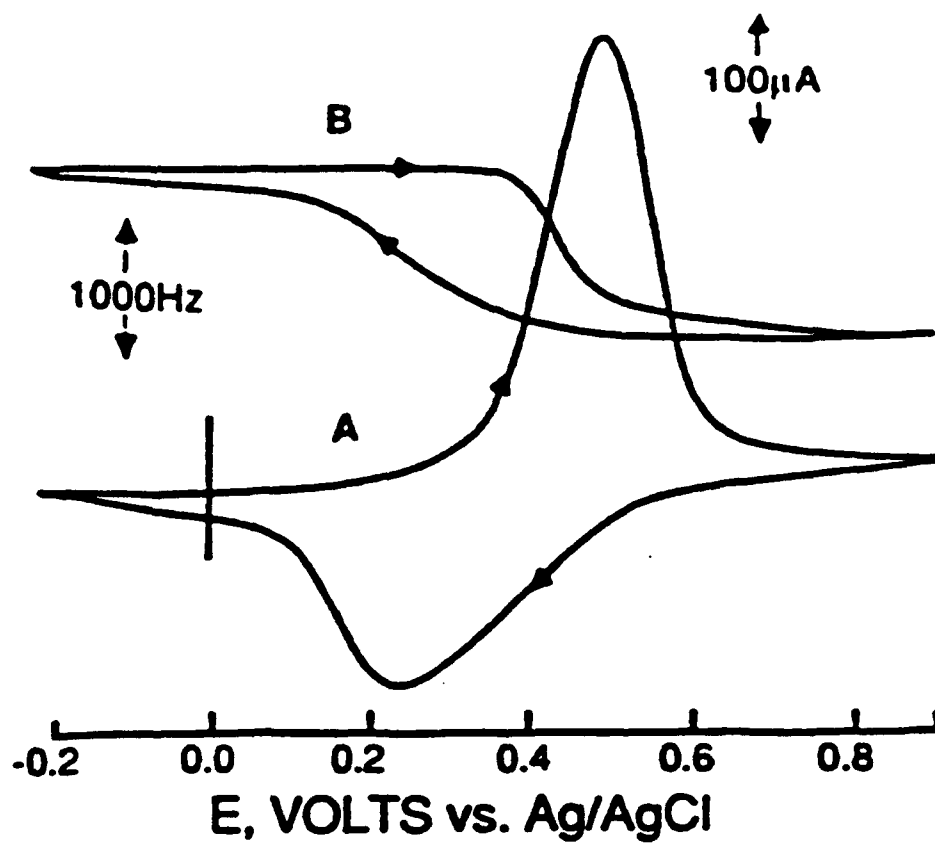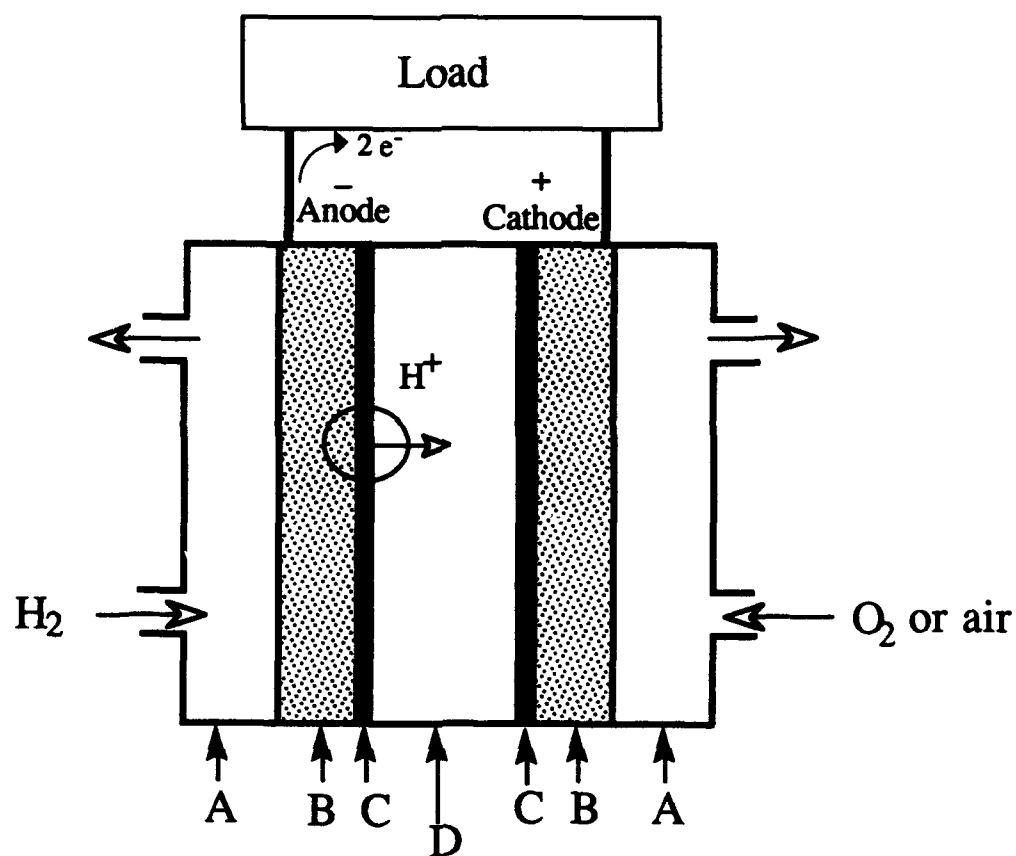
Figure 8 Curve A: Cyclic voltammogram of polyvinylferrocene (PVF) on gold in 0.1 M KPF_6. Scan rate 10 mV sec^{-1}. Curve B: EQCM frequency curve obtained simultaneously with Curve A. from reference 84.

A: Gas Manifolding
B: Porous Graphite Block
C: Active Catalyst Layer (dispersed Pt and Teflon binder)
D: Polymer Electrolyte

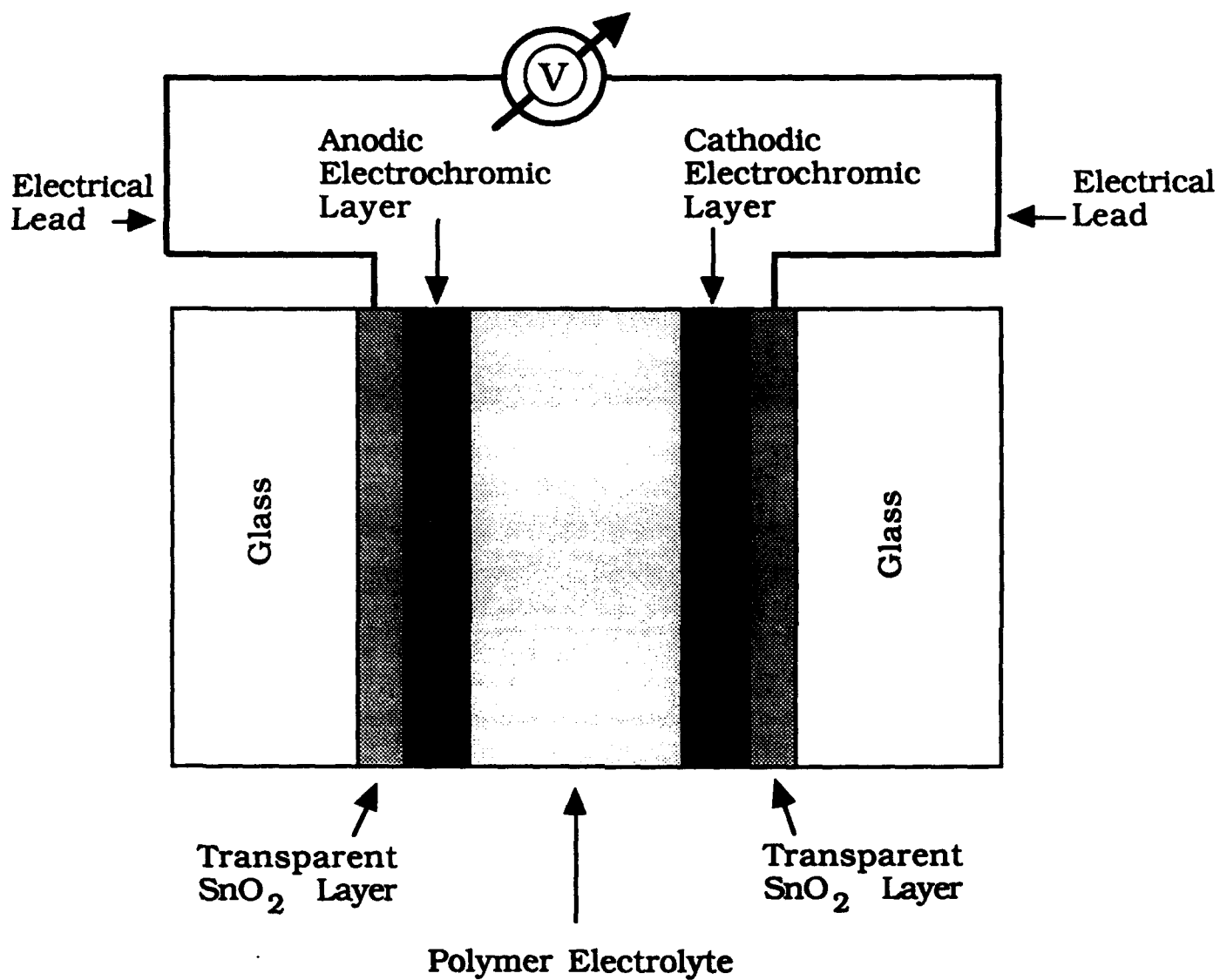**Figure 9**: Schematic diagram of a Polymer Electrolyte Fuel Cell

Figure 10. Schematic Diagram of a "smart window".